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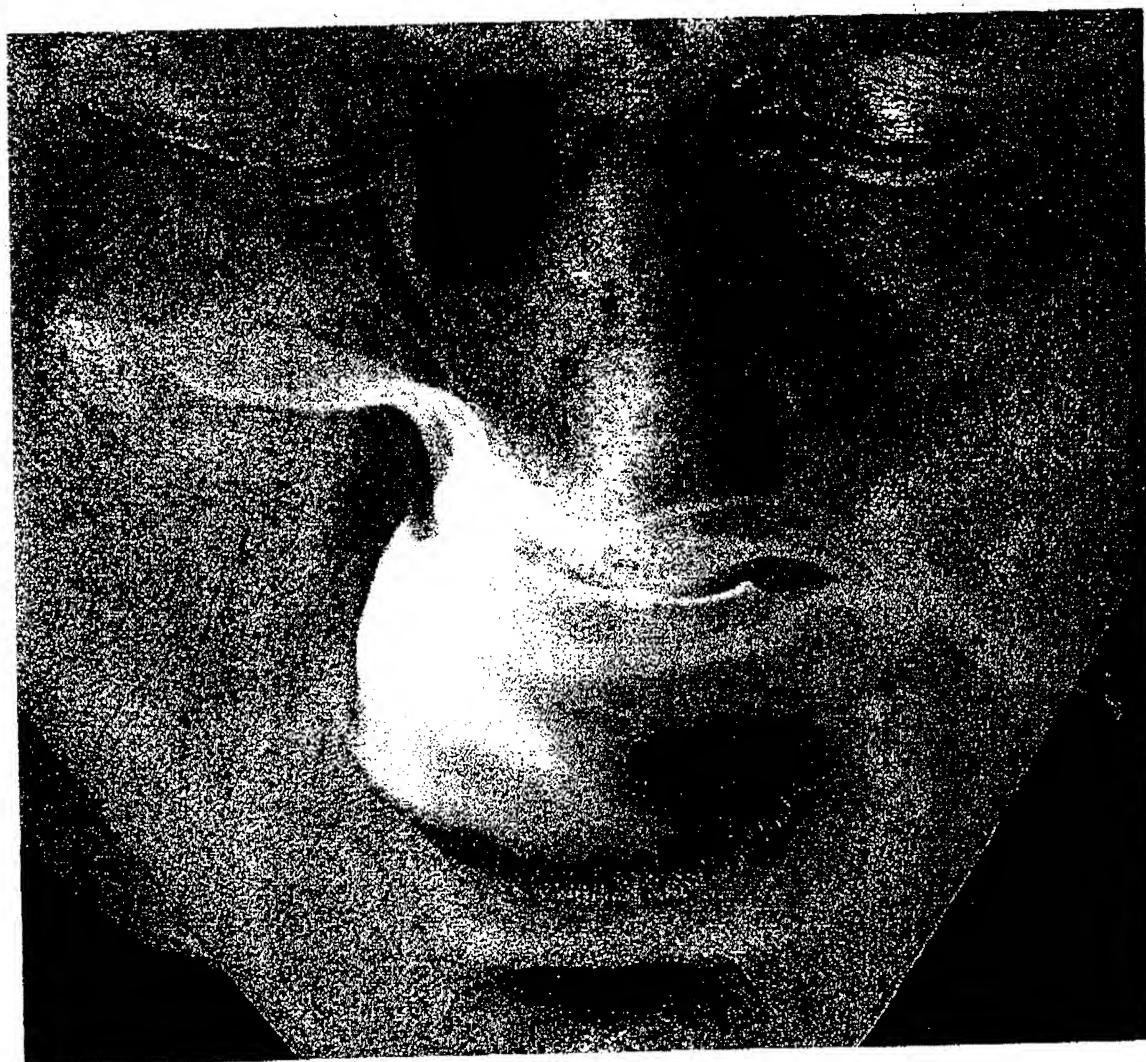
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What found the top quark.

Archaeology in peril.

The Niels Bohr mysteries.

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*Clouds of tobacco smoke continue
their spread, despite warnings.*



Dendrimer Molecules

*Chemists can now build fractal supermolecules.
This new class of polymers promises to be valuable
in biotechnology and environmental protection*

by Donald A. Tomalia

In the center of Michigan, along the Chippewa River, some 130 miles southeast of Sleeping Bear Dunes National Lakeshore, the land is not productive enough for traditional agriculture, but it is adequate for growing trees. Thousands of trees of all types, with every branching pattern and shape imaginable, flourish there. Year after year young seedlings with single trunks emerge. Then their trunks elaborate branches, and those branches produce more branches in the same way, giving rise to the lush and varied forest.

As I pondered these trees near my home some 20 years ago with the eyes of a chemist, the systems of branches made me wonder whether one could design large, precisely defined molecules by adding branch after branch onto some original substance. The idea of gaining such control over the formation of a molecule appealed to me immediately on both theoretical and practical grounds, but it was not until the end of the 1970s that I found a way to put the concept into practice. Today my technique and other similar approaches are making it possible to construct tree-like molecules that mimic a variety of biological structures, including proteins. There is good reason to believe that these synthetic constructions

will prove valuable in medicine, the electronics industry and other fields.

Long ago nature devised exquisite strategies for manipulating the structures of the molecules necessary for initiating and sustaining life. Chemists have tried for years to achieve such mastery over the structures they create. Organic chemists have gained substantial command over the synthesis of small complex molecules. But the goal of constructing large well-defined molecules has been more elusive.

The idea of directing molecular growth to make these extremely large molecules with useful properties derived from experiments done in the 1930s, when Hermann Staudinger, then at the University of Freiburg, managed to link identical subunits, or monomers, into strings of spaghetti-like molecules called random-coil polymers. Staudinger's work represented the first successful attempt at assembling large molecules from well-defined smaller components. But the investigator had little control over the lengths of the polymers, which spanned the continuum from microscopic (on the nanometer scale) to macroscopic (on the millimeter or centimeter scale). These polymers turned out to have interesting and valuable features; indeed, many familiar items are made of these types of random-coil polymers, including Styrofoam insulation, polyethylene milk cartons and Plexiglas.

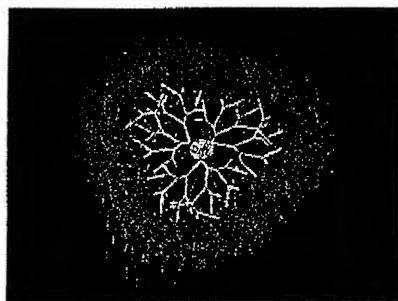
About 10 years later Paul J. Flory, then at Cornell University, and Walter H. Stockmayer, then at the Massachusetts Institute of Technology, took another step toward making large molecules. They developed a second class of polymer that is formed by bridging, or cross-linking, random-coil polymers at various sites on the long chains. The loops and connections give rise to inflexible three-dimensional structures referred to as cross-linked polymers. Their rigidity makes these substances insoluble in most liquids and therefore

useful as coating materials on fiberglass hulls of boats or in urethane foams and epoxy systems.

In both random-coil and cross-linked polymers, monomers are joined into long, meandering chains of molecules having varying lengths and sizes, and the precise internal arrangements are impossible for chemists to predetermine. My idea in the mid-1970s was to gain such control. I finally figured out how to achieve that objective after making a surprising discovery in 1979.

Just Add Methanol and Stir

One spring day colleagues in my laboratory and I were following our standard procedure for making linear random-coil polymers called polyamidoamines. Although typically the synthesis did not require a solvent, on this particular day we added one—methanol (CH_3OH)—to the initial set of ingredients in order to facilitate stirring. We did not expect methanol to alter the substances in this reaction chemically.



STARBURST DENDRIMERS, shown at the right and in cross section above, have an ammonia molecule at their core. These dendrimers consist of three branched "trees," parts of which are highlighted in the cross section. The trees were systematically built onto the core through an iterative process developed by the author and his colleagues.

DONALD A. TOMALIA is a research professor and director of nanoscopic chemistry and architecture at the Michigan Molecular Institute in Midland. He received his bachelor's degree in chemistry from the University of Michigan, Flint College. In 1968, while working as a synthetic polymer chemist in Dow Chemical Company Research Laboratories in Midland, Tomalia completed his Ph.D. in chemistry at Michigan State University. He is a cofounder, director and the chief scientist of Dendritech, Inc. His major areas of interest are in structure-controlled polymers, molecular recognition and nanoscopic chemistry.

The rest of the process went along as usual: we mixed the monomer methyl acrylate ($C_4H_6O_2$) with ethylene diamine ($C_2H_8N_2$).

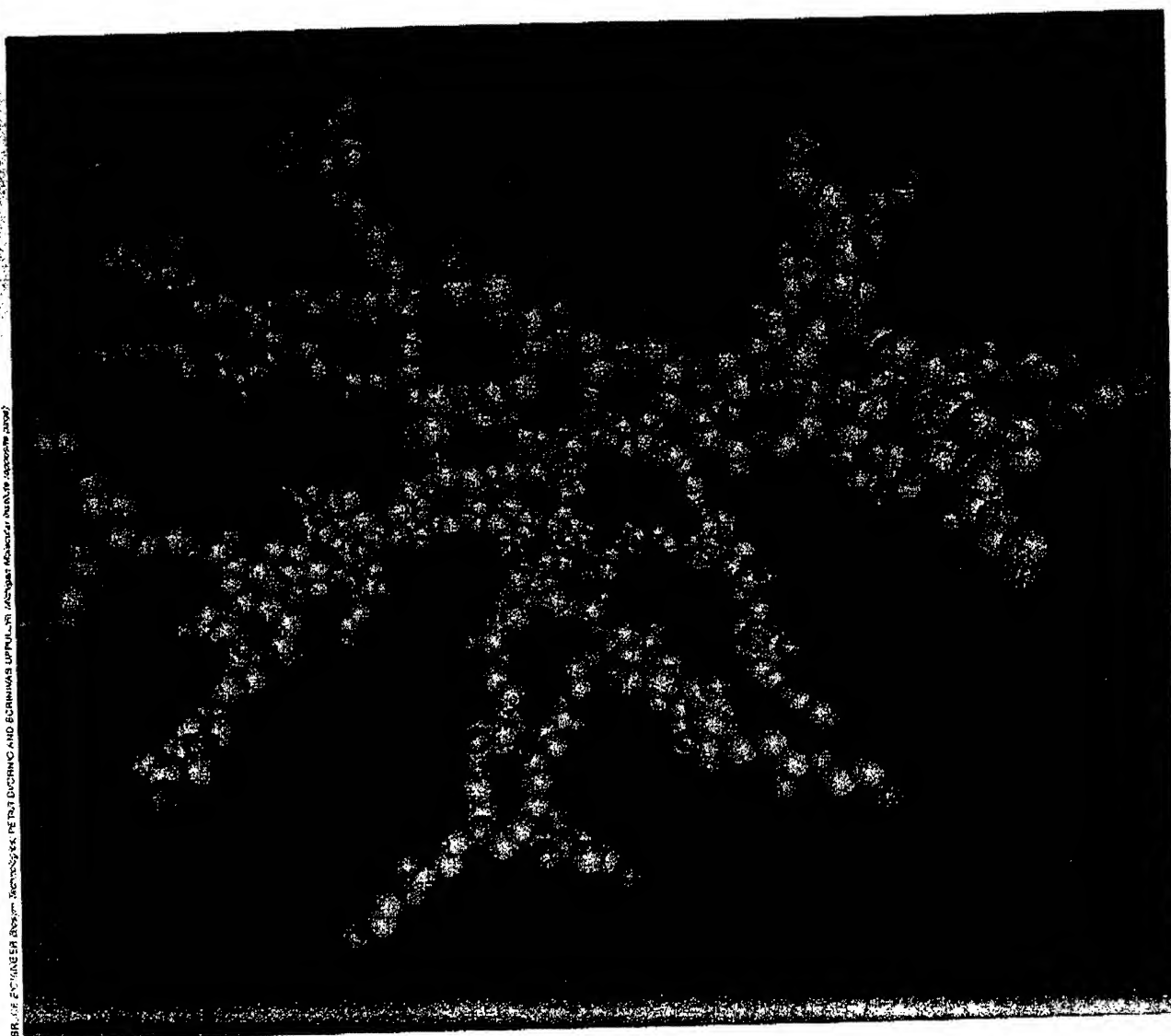
Much to everyone's amazement, we did not get the same random-coil polymer we usually made. Normally, when we mixed these two chemicals, they linked together in a one-to-one ratio, which resulted in a long continuous strand consisting of alternating methyl acrylate and ethylene diamine components. Instead, when we determined the structure of the product from this reaction, we discovered a remarkable arrangement: there were no long strands, only discrete units consisting of two

methyl acrylate groups connected to each end of ethylene diamine. In this case the methanol did affect the reaction. It apparently facilitated the removal of hydrogen atoms from the nitrogens in ethylene diamine and enabled methyl acrylate to take their places.

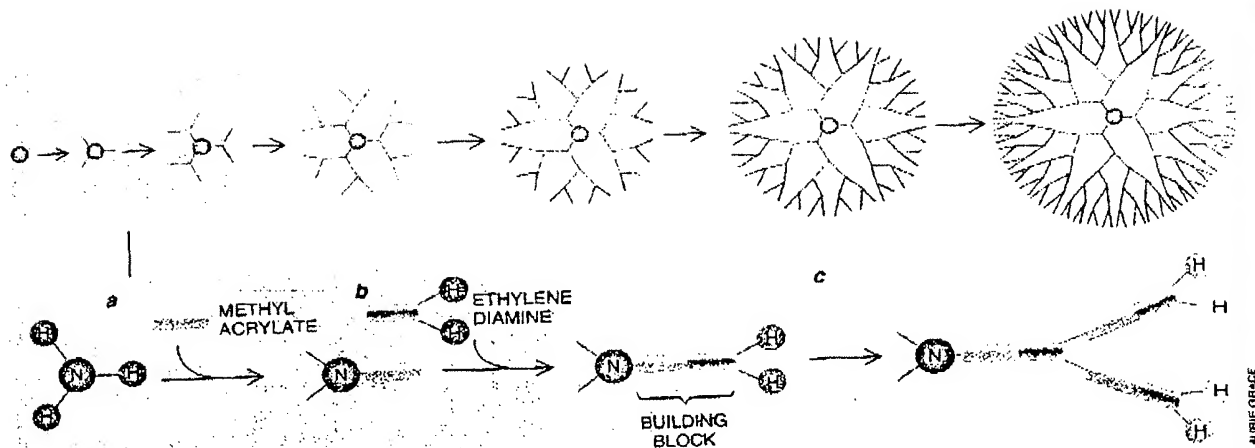
When we repeated the process—now adding ethylene diamine and methyl acrylate to the existing simple structures—we generated an even more intricate compound. This structure contained 12 methyl acrylate and five ethylene diamine monomers. I soon realized we might be able to adapt this technique to assemble the branching molecules I had envisioned back in the woods

of Michigan. These molecules would be quite different from the long chains of monomers found in classical random-coil and cross-linked polymers.

Staring at the pattern of those trees, I had specifically imagined a system of molecular growth that resulted in large symmetrical structures built in stages, much as seasonal branching of young trees leads gradually to the development of a broad assembly of branches in older trees. Onto one reactive site of an initial core molecule, a second, linear molecule could be added, producing a stem. Two additional molecules, similar to the linear one, could be attached to the free end of the second molecule,



BR. OF ETHYLENE DIAMINE AND METHYL ACRYLATE POLYMERIZATION. (METHYL ACRYLATE AND ETHYLENE DIAMINE MONOMERS)



GROWTH OF DENDRIMER proceeds by exponential addition to a core molecule (top). In this example, the core molecule contains one nitrogen atom and three hydrogen atoms (detail). First, the hydrogen atoms are replaced by a molecule called methyl acrylate (a), as is shown for just one of the three atoms. A second molecule—ethylene diamine—is added as well (b). Together the monomers constitute the basic building blocks of the dendrimer. The unattached end of this unit has two nitrogen-hydrogen bonds, and so the two steps can be repeated to affix two more sections to the growing structure (c). Now the unattached end has four nitrogen-hydrogen bonds, allowing four units to be attached subsequently. Repetition of the process gives rise to the intricate final structure. (Blue coloring highlights the fractallike growth.) The well-defined architecture contrasts with the irregular structure of a random-coil polymer (left).

producing a Y-shaped structure. Reiteration of this pattern, adding at least two more of these molecules to the tips of each added Y, would quickly lead to an ordered system of monomers.

This basic approach has resulted in the creation of an entirely new class of polymer architecture, in which concentric tiers of monomers—resembling the layers of an onion—are assembled around a single molecule (the initiator core molecule) at the center. As the layers build outward from this core molecule, the fractal, or dendritic, nature of the growing structure emerges: large regions resemble the smaller Ys formed by triplets of monomers. At the same time, the internal structure takes on a starlike appearance. We thus call the final products "Starburst dendrimers."

Adjustable Properties

We created our first dendrimers by repeatedly performing two simple operations that we still use to this day. When assembling dendrimers, we generally start with an ammonia molecule, which consists of a central nitrogen atom linked to three hydrogen atoms. To this molecule we add enough methanol to facilitate substitution of methyl acrylate for all three hydrogen atoms of the ammonia molecule. Next we add the second monomer, ethylene diamine, which attaches to the free end of each of the three methyl acrylate compo-

nents. Because ethylene diamine has an amine (NH_2) group at its unbound terminal, all three branches on the central ammonia group now end in a nitrogen atom from which two hydrogen atoms protrude. In other words, the three outermost tips resemble the ammonia molecule at the core, except that six instead of three hydrogen atoms are available to react with additional methyl acrylate monomers.

Just as we are able to replace all three hydrogen atoms in ammonia with three methyl acrylate monomers, we are able to replace the six hydrogens from the three amine groups with six monomer units. To be more precise, in this second iteration of the two-step process, we attach six methyl acrylate molecules to the expanding structure and link ethylene diamine to each of the monomers. These six ethylene diamine-linked monomer groups—forming what we call the second generation of the dendrimer—provide 12 hydrogen atoms to start the third generation. Each successive generation exponentially increases the number of hydrogen atoms available to react.

We soon found that this approach, known as amplification chemistry, can be repeated through as many as nine or 10 generations, until the structure runs out of room to hold additional monomers in perfect branches. The procedure can yield enormous macromolecules, some of which have masses over a million times that of hydrogen (which has

an atomic mass of one) and diameters more than 300 times that of hydrogen. And the outermost surface can carry hundreds or even thousands of reactive molecules, known as functional groups. These groups might be derived from the same monomers used to build the dendrimer, or they might be different functional groups, depending on the requirements of the intended application.

Because dendrimers have very regular and predictable patterns of growth, chemists can manipulate the characteristics not only of the interior of the molecule but also of the outer surface. Hence, they can additionally regulate the way the molecule chemically reacts with other molecules. In short, we can specify the size, shape and reactivity of the dendrimers, which allows us to manipulate the properties of the macromolecules we make to an extent that was not possible before.

Indeed, the adjustable physical and chemical properties of dendrimers are their most striking features. Chemists gain this control by carefully selecting the reactants used for making dendrimers. For example, the overall size of a dendrimer is determined by the number of generations included, the length of the monomers used in each generation and the angles between the monomers—features that depend on the chemical makeup of these molecules.

The final structure can also be shaped by the choice of the initiator core mole-

cule. Although the first dendrimers were built from an ammonia core, we have since explored derivatives of ammonia as well as completely different families of compounds, including phosphorus-containing or silicone-containing molecules, benzene (C_6H_6) rings and carbon chains (which have hydrogen and sometimes oxygen atoms attached to them). Each different combination of core molecule and monomers results in a unique dendrimer structure with distinct properties. For instance, if we start with a molecule derived from ammonia but with only one available hydrogen atom, the dendrimer will resemble a mushroom cap. With two active hydrogens, the dendrimer looks more like a kidney-shaped molecule rather than the symmetrical spheroid that is obtained from a pure ammonia core.

As often happens in science, we were not the only researchers to discover a way to build branched molecules. Fritz Vögtle of the University of Bonn and his team were also investigating the possibility of constructing branched molecules around the same time. After we produced our first dendrimers, we learned that Vögtle's group had used a type of amplification chemistry similar to ours to synthesize small branched molecules. The other team's structures consisted mainly of derivatives of ammonia linked by the monomer acrylonitrile. The German researchers called their products "cascade molecules." Other German and Dutch investigators more recently showed that by using a different catalyst in the procedure, the Vögtle approach could be adapted for making large dendrimers as well.

Since 1979 many groups have used methods similar to ours and Vögtle's to synthesize these dendritic supermolecules. In 1985 George R. Newkome of the University of South Florida pioneered an alternative type of amplification chemistry to produce treelike molecules, which he referred to as arborols.

Another interesting approach to dendrimer synthesis was described in 1989 by Jean M. J. Fréchet and Craig J. Hawker of Cornell University and, separately, in 1990 by Timothy M. Miller and Thomas X. Neenan of AT&T Bell Laboratories. Instead of using the so-called divergent method—starting from the inside and building outward—as our laboratory does, these chemists used what is known as the convergent method of synthesis. They constructed individual branches first and then attached the units to a central core molecule.

Between 1980 and 1990 fewer than a dozen papers were published on this subject, but in the past several years

there has been an explosion of activity. More than 20 types of dendrimer families with more than 100 different surfaces have now been reported. Apparently, a wide variety of monomers—including metals—may be used to create dendrimers. Moreover, it seems that virtually any functional group that can be found in an organic chemistry textbook can be attached to the surface of dendrimer molecules to carry out selected tasks.

Parallels in Nature

Chemistry is not just about connecting and rearranging atoms in various ways. It is a philosophy, a way of thinking about the dimensional hierarchy of the universe, from the simplest atoms to the most complex molecules and phenomena. The order in atoms and molecules is echoed everywhere in nature, from the branching schemes of trees and coral reefs to the dendritic networks of airways in the lungs and blood vessels in the circulatory system. The significance of these pervasive patterns is not entirely clear, but such connections are fascinating to contemplate.

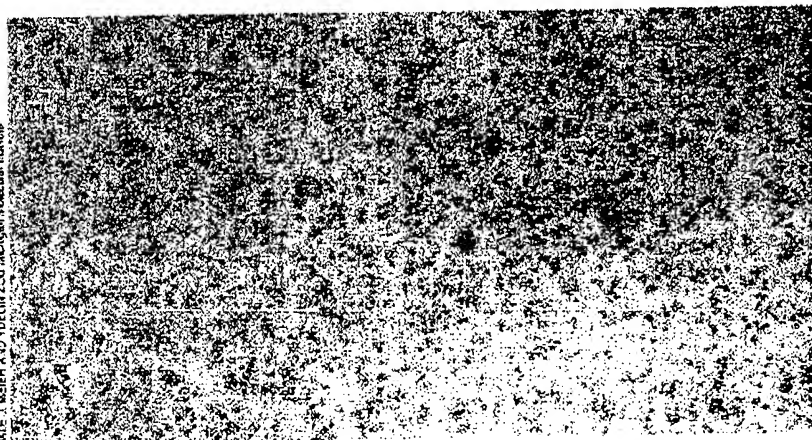
For example, dendrimers have many intriguing organizational similarities to atoms. As dendrimers or atoms form, curious geometric or arithmetic patterns usually develop. These schemes may involve various repetitive structures or regular sequences of numbers. For example, the number of monomers in a dendrimer with an ammonia core increases in a well-defined sequence: 3, 6, 12, 24, 48 and so on. In this way, concentric dendrimer amplification resembles the accumulation of electrons in successive elements of the periodic

table. The number of electrons within each orbital of an atom is also limited. The innermost electron cloud of an atom may not contain more than two electrons; the first generation in an ammonia-based dendrimer may not contain more than its saturation value of three monomers.

Additional parallels can be drawn between the branching network inside dendrimers and certain patterns of biological development. Dendritic growth in these molecules resembles the exponential growth seen during cell mitosis, the process in which one cell becomes two, two cells become four and so on. Furthermore, the original core of the dendrimer determines its final structure, just as the characteristics of the dividing cells derive their unique features from the genetic makeup of the original cell.

The similarities between dendrimers and atoms (the fundamental building blocks of nature) and the parallels between dendritic and biological development may well have practical implications. They suggest that individual or even larger assemblages of the structures might eventually be exploited as synthetic replicas of biological molecules. This notion is reinforced by the fact that dendrimers are about the same size as some of the most important molecules in nature, including enzymes, antibodies, DNA, RNA and viruses.

Scientists have frequently marveled at the way living systems outdo our most advanced techniques for manipulating and combining atoms into large biological molecules. Although dendrimers represent only one of several approaches to building molecules in this



INDIVIDUAL DENDRIMERS (black dots), each about 11 nanometers across, can be seen with an electron microscope. They are similar in size to many large biological molecules. Dendrimers can also be assembled into much bigger clusters.

size range, it seems clear that these structures will function as the basis for what I like to call a new, nanoscopic chemistry set for constructing complex molecules that mimic biological compounds in size, shape and function.

One of the many exciting indications that dendrimers can have practical uses has recently come from my laboratory and that of James R. Baker, Jr., of the University of Michigan Hospital and, separately, from the laboratory of Francis C. Szoka, Jr., of the University of California at San Francisco. We have found evidence that dendrimers might one day be valuable in gene therapy, as vehicles for bringing DNA sequences into cells.

Dendrimers Deliver DNA

The DNA-transporting structures we fashioned resemble clusters of proteins called histones. In the human body, nuclear DNA is found wrapped around such clusters. Our dendrimers are so close in shape and size to a histone cluster that DNA wraps around them just as it does around the natural protein complex. The DNA we studied contained a genetic sequence that codes for the protein luciferase, the substance that gives fireflies their luminescence. This gene is rather easy to track: when it is successfully transferred to a new cell and remains functional, the cell begins to glow.

In petri dish experiments, we combined histonelike dendrimers and the luciferase gene with close to 30 different types of cells from various species,

including humans. In nearly all cases, the dendrimers transported genetic materi-

al into the cell and gave rise to the luciferase protein. (We do not yet completely understand how the dendrimer-DNA unit makes its way into cells.)

We have other reasons for suspecting that dendrimers might be of service in gene therapy. Notably, the structures can be designed to home in on specific target cells. For example, attaching certain substances, particularly sugar and protein groups, to dendrimer surfaces causes these polymers to adhere more favorably with some cell membranes than with others. By carefully selecting the components we add, we can direct a dendrimer-DNA combination to specific types of cells.

Furthermore, dendrimers may have an advantage over the current method of delivering genetic material to cells. Today scientists often use modified viruses to bring genes to cells. Unfortunately, the viruses can stimulate an immune response that destroys the viral agents before the genetic material reaches its intended site. If the immune response is severe, it can actually endanger the patient. Dendrimers have not

FURTHER READING

STARBURST DENDRIMERS: MOLECULAR-LEVEL CONTROL OF SIZE, SHAPE, SURFACE CHEMISTRY, TOPOLOGY, AND FLEXIBILITY FROM ATOMS TO MACROSCOPIC MATTER. Donald A. Tomalia, Adel M. Naylor and William A. Goddard III in *Angewandte Chemie, International Edition in English*, Vol. 29, No. 2, pages 138-175; February 1990.

RISING CHEMICAL "STARS" COULD PLAY MANY ROLLS. Joe Alper in *Science*, Vol. 251, pages 1562-1564; March 29, 1991. DENDRIMERS, ARBOROLS, AND CASCADE MOLECULES: BREAKTHROUGH INTO GENERATIONS OF NEW MATERIALS. Hans-

Bernhard Meckelburger, Wilfried Jaworek and Fritz Vögel in *Angewandte Chemie, International Edition in English*, Vol. 31, No. 12, pages 1571-1576; December 1992.

FUNCTIONAL POLYMERS AND DENDRIMERS: REACTIVITY, MOLECULAR ARCHITECTURE, AND INTERFACIAL ENERGY. Jean M. J. Fréchet in *Science*, Vol. 263, pages 1710-1715; March 25, 1994.

STARBURST/CASCADE DENDRIMERS: FUNDAMENTAL BUILDING BLOCKS FOR A NEW NANOSCOPIC CHEMISTRY SET. D. A. Tomalia in *Advanced Materials*, Vol. 6, Nos. 7-8, pages 529-539; July-August 1994.

triggered such an extreme response in any of our laboratory studies. Many research teams are also developing techniques for transporting other kinds of molecules, such as drugs, to selected targets in the body.

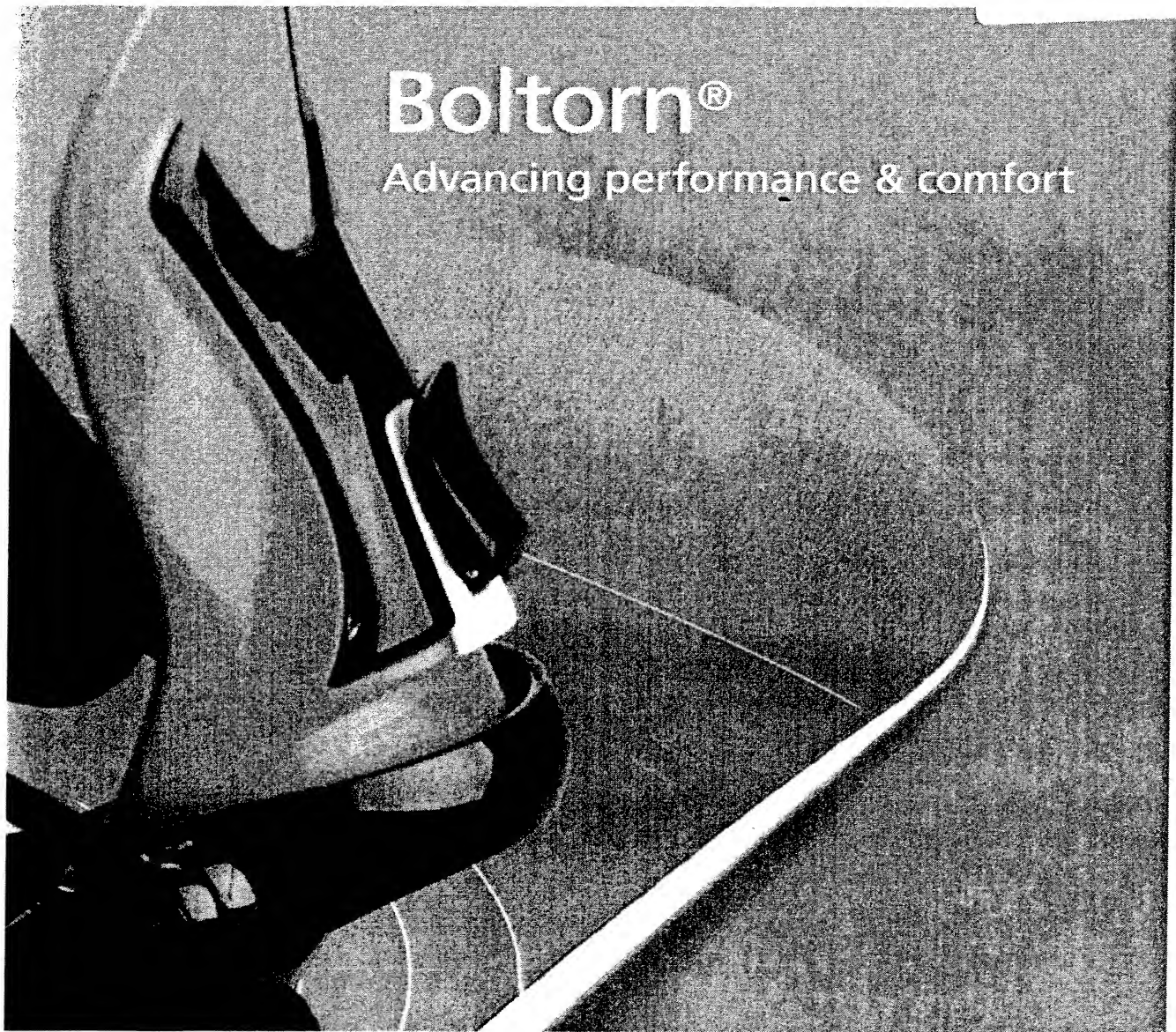
Last December, Gerard van Koten and his group at Utrecht University in the Netherlands identified another application for dendrimers that could have great significance for the chemical industry. In many manufacturing processes, chemical plants must use catalysts to enhance the efficiency of certain reactions. The outside of a dendrimer can be covered with many catalytic sites, so that one dendrimer can induce a large number of catalytic reactions. These dendrimers typically dissolve in the reaction mixture readily, which further facilitates catalysis. Additionally, the large size of the structures should allow the dendrimers to be easily recovered from a reaction mixture by filtration methods; the dendrimers can then be used again.

The ability to attach substances that can serve as catalysts or biosensory agents to the surface of dendrimers has attracted the attention of the U.S. Army Research Laboratories. In collaboration with H. Dupont Durst and his colleagues there, we are studying the possibility of using dendrimers to detect dangerous biological or chemical agents in the environment.

Whether in the chemical industry, in the pharmaceutical field or in environmental defense applications, dendrimers show great promise as supermolecules whose properties can be made to order. We look forward to exploring the full potential of this versatile and intriguing new class of polymers.

DNA WRAPS AROUND selected dendrimers in a manner that resembles the way it twists around clusters of proteins known as histones in the nuclei of cells. This property is one of several suggesting that dendrimers may be useful in gene therapy, as vehicles for delivering altered genes to cells.

TIMO BERGMANN



Our dendritic polymers

- ◆ Secure exceptional firmness and comfort in flexible polyurethane foam
- ◆ Improve the Tg/flexibility ratio of cast polyurethane elastomer products
- ◆ Ensure rapid curing, excellent durability and low toxicity in UV curing applications
- ◆ Provide reduced VOC and improved performance in architectural coatings

The elements of success

You need a partner who can see the big picture when it comes to your products, your processes and your customers. Our experience and expertise in the special niches of organic chemistry, process technology and application development are at your service, providing you with a complete chain of solutions to enhance quality and profitability at every step.

Our versatile intermediates, an essential element of your winning formula, are specifically designed to add value and enhance end-product performance. Your solution to meeting the increasing demands for safer, lighter, more durable and environmentally friendly end-user products, begins here.

Innovation in everything we do

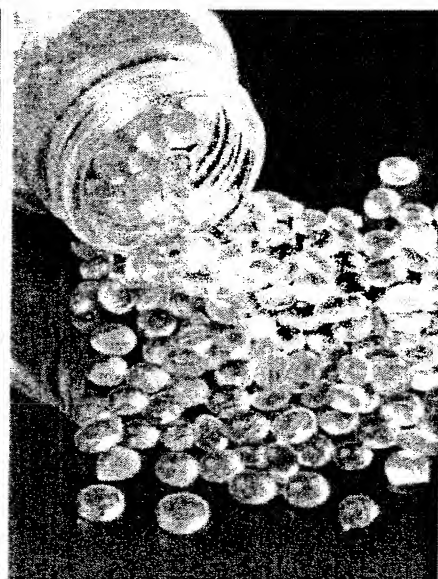
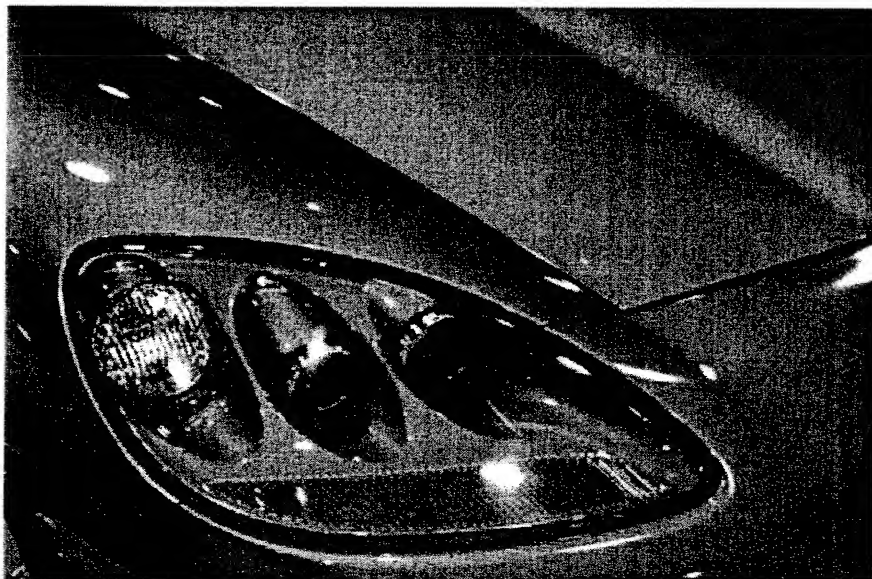
Innovation distinguishes every aspect of our business process. Developing smarter and safer solutions creates real value in new chemical applications. Focused innovation instills leadership and purpose in our business activities, improves internal processes and increases application and product competitiveness.

Delivering our promises globally

Our global presence provides you with reliable solutions and processes, consistent high quality, security of production and supply and delivery with precision. This commitment also means rapid response when product or application support is required and the very best in technical support.

Putting the care into chemicals

We take our responsibilities to heart and are committed to attentive, sustainable business practices. We minimize risks for our customers, our employees and the environment by working proactively to ensure safe products and processes.



Advancing performance & comfort

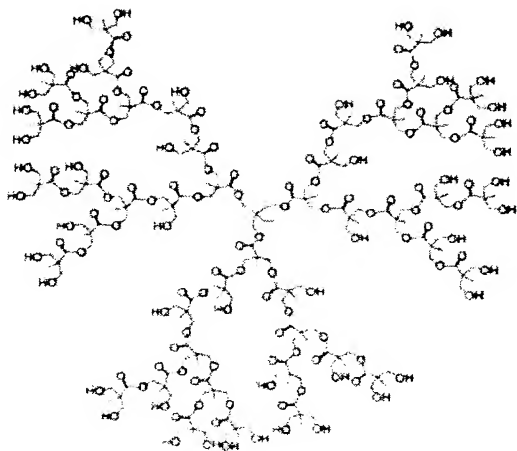
Sharpen your competitive edge by partnering with the global leader in bringing cost-effective dendritic polymers to the market. Dendritic polymers are characterized by a densely branched backbone and a large number of reactive groups. Their globular structures have excellent flow and processing properties at high molecular weight. The exceptional concentration of reactive groups facilitates customization of properties for a wide range of end uses.

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- ◆ Performance additives for flexible polyurethane foam such as in automotive seating applications.
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Boltorn® technology

- ◆ Large number of primary hydroxyl groups
- ◆ Densely branched polymer backbone
- ◆ Extensive formulation possibilities



The cutting edge of technology

Our Boltorn® products are produced using polyalcohol cores, hydroxy acids and technology based on captive materials. The dendritic structures are formed by polymerization of the particular core and 2,2-dimethylol propionic acid (Bis-MPA). The base products obtained are hydroxyl-functional dendritic polyesters. Fully aliphatic and consisting only of tertiary ester bonds, they provide excellent thermal and chemical resistance. Extensive branching also improves reactivity, lowers viscosity and results in balanced mechanical properties. Five base products are available as polymer building blocks and elastomer cross-linkers representing a range in molecular weight, hydroxyl functionality, glass transition temperature (Tg) and polarity.

Our dendritic base products:

Boltorn® H20

16 terminal hydroxyl groups,
nominal molecular weight of 1,750 g/mol

Boltorn® H2003

12 terminal hydroxyl groups,
nominal molecular weight of 2,300 g/mol

Boltorn® H2004

6 terminal hydroxyl groups,
nominal molecular weight of 3,100 g/mol

Boltorn® H30

32 terminal hydroxyl groups,
nominal molecular weight of 3,600 g/mol

Boltorn® H40

64 terminal hydroxyl groups,
nominal molecular weight of 7,300 g/mol

We welcome your questions. More detailed information and specifications of each product are available on www.perstorp.com or through your Perstorp sales representative.

Fine-tuning with polyols

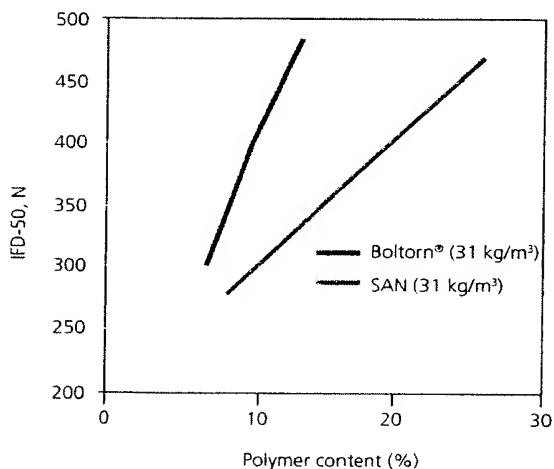
Boltorn® for polyurethanes

Millions of car owners already enjoy superior seating comfort with the help of Boltorn® technology. In partnership with a leading automotive foam supplier, we have developed a unique technology that improves the firmness of high-resilience foam articles with dendritic polymer polyols.

Boltorn® H311 – for exceptional firmness & stability

This liquid polymer polyol provides exceptional compressive load-building characteristics in flexible foam at very low addition levels. It is used as an additive, partially replacing conventional cross-linkers or graft co-polymer polyols of SAN-type. Compared to conventional technology, Boltorn® H311 offers considerable benefits:

- Two to three times the efficiency in providing compressive loads (IFD or CFD) at a given addition solids level, which allows lower average solids levels to be used.
- Exceptional firmness, extending beyond current state-of-the-art technology.
- Improved foam stability due to the cross-linking mechanism and reduced surface voids of finished parts.



Compressive load as function of polymer content for Boltorn® H311 vs. co-polymer polyols

Boltorn® P500 – new release for high firmness at low compression set

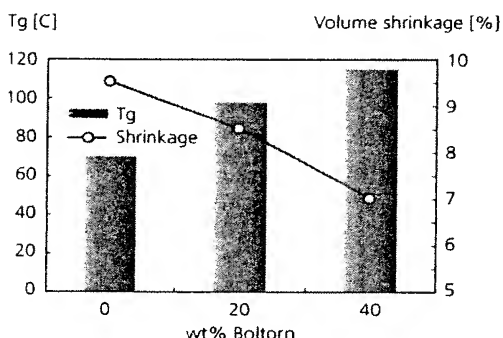
Our newly launched dendritic polymer polyol for molded foam is a liquid water-free product that yields exceptionally low compression set at high firmness when used with graft co-polymer polyols. The low compression set allows you to operate at reduced foam density and still meet the comfort specifications of end users.

Formulation	60-5	60-15	50-11-4
Polyol (Hyperlite 1656), pph	87.95	63.85	63.51
Co-polymer polyol (Hyperlite 1650), pph	12.05	36.15	36.49
Boltorn® P500, pph	0	0	4.19
DEOA-LF, pph	0.50	0.50	1.00
Glycerine, pph	0	0	0
H ₂ O, pph	1.76	1.75	2.21
DABCO 33-LV, pph	0.10	0.10	0.36
NIAX A-1, pph	0.08	0.08	0.08
PC77, pph	0.20	0.20	0.00
Y10184, pph	1.00	1.00	0.70
TDI 80, pph	23.61	23.12	33.72
Total wet weight, g	127.25	126.75	142.26
Total dry weight, g	119.60	119.10	130.75
SAN, %	5	15	11
Boltorn® P500, %	0	0	4
Density, kg/m ³	60	60	50
IFD-25, N	147	239	192
IFD-65, N	390	633	558
Dry set, %	4	4	2.9

Density reduction at reduced compression set when using Boltorn® P500

Cross-linkers for increased durability

We offer you two dendritic polyester polyols suitable as cross-linkers for cast polyurethanes and elastomers. Boltorn® H2003 is a polyol of relatively high molecular weight and high hydroxyl value. Added to a polyurethane formulation, it improves the Tg and Shore-hardness of some formulations with aliphatic isocyanates. Boltorn® H2004 is a liquid product with hydrophobic chain stoppers that is used to yield durable systems with high flexibility.



High molecular weight and functionality of acrylated Boltorn® oligomers improves hardness and Tg, yet reduces shrinkage and curl, when replacing polyether in polyether/PEOTA formulation

Boltorn® for radiation curing

Oligomer precursors for superior performance

Boltorn® products enhance radiation curing applications by providing oligomer precursors that significantly increase the average molecular weight of UV formulations at high acrylate concentration. Acrylates based on Boltorn® technology are typically used to partially or fully replace urethane acrylates, other top-end oligomers or acrylates of high functionality. Using Boltorn® dendritic polyols as starters for oligomer acrylates offers significant benefits:

- ◆ Excellent reactivity
- ◆ Improved scratch resistance and film hardness
- ◆ Low shrinkage and good adhesion
- ◆ Exceptional flow properties and good pigment wetting
- ◆ Improved labeling with low extractables
- ◆ Unique molecular weight/viscosity ratio

For coatings, the balance between flow and properties like reactivity, and chemical and scratch resistance, is crucial for meeting end-user demands. Environmental compliance is also a key competitive factor. Radiation curing systems, typically UV, have gained market share in the past decades as very rapid curing and excellent film properties are obtained with low or no VOC emissions.



Acrylated polyol	Di-Penta (DPHA)	Acrylate of Boltorn® P500
Viscosity, mPas, 100% solids, 23°C	14,000	700
Min. UV-dose, tack-free, mJ/cm²	200	200
Erichsen-flex., aluminum, mm	0.4	2.2
Pencil hardness, PC-Sheet, 250µm	3H/4H	2H/3H
Scratch resistance (200 rubs), gloss 60° ret., %	90	91
Tape adhesion on PC-sheet, 0-5, 5 best	2	5
Adhesion, 180° bending test	No	OK

Properties of acrylated Di-Penta and acrylated Boltorn® P500 – all coating formulations cured with 3% Irgacure 500 from Ciba at 12µm film thickness with a UV-dose of 500 mJ/cm² unless otherwise stated

Designed to enhance

Boltorn® for architectural coatings

Boltorn® resins – safer performance

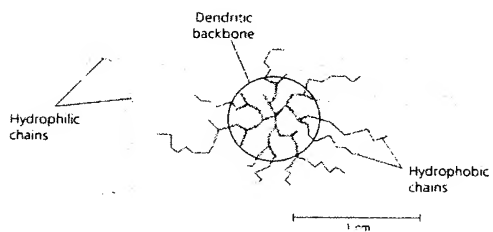
Our Boltorn® performance resins for solvent borne and water-borne architectural coatings help coating formulators comply with environmental demands without compromising coating performance. A number of patented technologies have been developed in which Boltorn® resins improve the performance of architectural coatings. Achieve excellent properties including reduced VOC, improved drying of woodstains and conversion of conventional solvent borne resins to waterborne equivalents.

Boltorn® U3000 – unique flow properties

For high-solid alkyds, the branched structure of Boltorn® U3000 provides unique flow properties, which allows woodstains and alkyd paints for outdoor applications to comply with recent VOC demands while still securing rapid drying and durability.

Boltorn® W3000 – efficient & powerful by design

The unique structure of dendritic polymers offers extensive design possibilities. We have developed Boltorn® W3000, a dispersing resin for converting conventional solvent borne alkyd paints into waterborne equivalents. The amphiphilic dendritic structure of Boltorn® W3000 contains both non-ionic water-dispersible and hydrophobic air-drying groups. The result is a powerful high molecular weight surfactant, which also contributes to drying and film properties.



Schematic structure of Boltorn® W3000

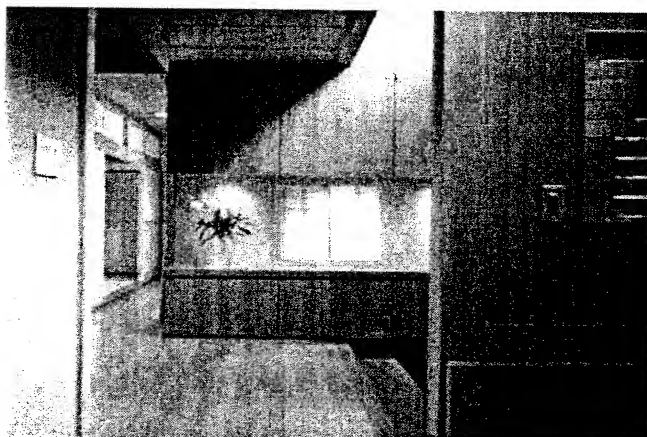
Formulation	Conventional woodstain	40wt% Boltorn® U3000
Type	oil/alkyd	oil/alkyd/dendritic alkyd
VOC, g/l	595	238
Viscosity, 23°C, mPas	28	72
Drying properties (45µm dry film)		
Film hardness-1 day, Ks	5	45
Film hardness-10 days, Ks	27	35
Film hardness-17 days, Ks	27	33
Film hardness-31 days, Ks	26	33

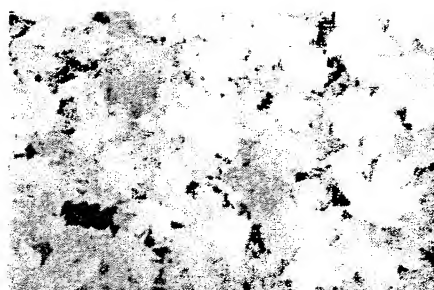
Effect on VOC and drying properties when adding Boltorn® U3000 to a conventional woodstain available in Scandinavia

High gloss paint for brush application	Boltorn® W3000 stabilised OL 65 alkyd emulsion	Solvent borne OL 65 alkyd (ref)	Conventional OL 65 alkyd emulsion
Boltorn® W3000, wt% in paint	2.3	-	-
Alkyd (OL65), wt% in paint	21.4	34.4	-
Alkyd OL65-internally emulsified	-	-	31.8
Solids content, wt%	49	67	51
PVC	17	17	13
VOC, g/l	0	270	0
Gloss, 60°	93	92	95
Drying*			
Dust-dry, h	0.5	0.5	0.5
Tack-free, h	4	3	1.5
Through dry, h	5	3.5	15.5
Hard, h	14	5	> 24

* Beck-Koller, glass panels at 23°C, 50% humidity, 25 µm DFT

The physical properties of a waterborne paint containing Boltorn® W3000 compared to a solvent borne counterpart and a conventional alkyd emulsion paint





Your Winning Formula

The Perstorp Group is the world leader in several sectors of the specialty chemicals market. Few chemical companies in the world can rival its 125 years of success. Today we have a rich performance culture distilled from our long history and extensive knowledge in the chemical industry. That culture and knowledge base enables us to produce Winning Formulas for a wide variety of industries and applications.

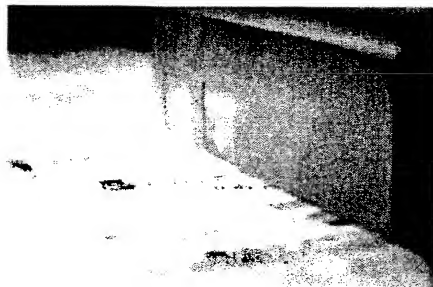
Our products are used in the aerospace, marine, coatings, chemicals, plastics, engineering and construction industries. They can also be found in automotive, agricultural feed, food, packaging, textile, paper and electronics applications.

Our production plants are strategically located in Europe, North America and Asia and are supplemented by sales offices in all major markets. We can offer you a speedy regional support and a flexible attitude to suit your business needs.

If you want a chemical partner who can offer you focused innovation to enhance your product or application, which is delivered reliably and responsibly look no further. We have a winning formula waiting for you.

Product data summary

Product	Soluble in	Appearance	Functionality	OH-value mg KOH/g	Mw (GPC) g/mol	T _g (DMA) °C	Viscosity Pas (°C)
Polymer building blocks & CASE polyols							
Boltorn® H20	NMP, Diglym Acetone, Glycols	Opaque pellets	16	490 – 520	2,100	25	6 (110)
Boltorn® H2003	EtOH, MEK, Toluen	Transparent	12	280 – 310	2,500	-5	1 (110)
Boltorn® H2004	EtOH, Toluene, Xylene	Yellow liquid	6.4	110 – 130	3,200	-35	15 (23)
Boltorn® H30	MeOH, Acetone, NMP	Opaque pellets	32	490 – 510	3,500	35	40 (110)
Boltorn® H40	MeOH, Acetone, MEK	Transparent pellets	64	470 – 500	5,100	40	80 (110)
Product	Soluble in	Appearance	Water cont. wt%	OH-value mg KOH/g	Mw (GPC) g/mol	T _g (DMA) °C	Viscosity Pas (°C)
Molded flexible foam							
Boltorn® H311	Polyether/ polyester polyols	Yellow liquid	9,5 – 10,5	235 – 255	5,500	-5	40 (23)
Boltorn® P500	Polyether polyols	Clear liquid	<0.5	560 – 630	1,800		12 (23)
Product	Soluble in	Appearance	Functionality	OH-value mg KOH/g	Mw (GPC) g/mol	T _g (DMA) °C	Viscosity Pas (°C)
Radiation curing							
Boltorn® H20	Acrylic acid + 15% toluene	Opaque pellets	16	490 – 520	2,100	25	6 (110)
Boltorn® H2003	EtOH, MEK, Toluen	Transparent	12	280 – 310	2,500	-5	1 (110)
Boltorn® P500	Acrylic acid + toluene	Clear liquid	hydroxyl	560 – 630	1,800	–	12 (23)
Boltorn® P1000	Acrylic acid + toluene	Clear liquid	hydroxyl	430 – 490	1,500	–	5 (23)
Product	Soluble in	Appearance	Functionality	OH-length % (wt/wt)	Mw (GPC) g/mol	Solids %	Viscosity Pas (°C)
Architectural, waterborne coatings							
Boltorn® U3000	Oils, coalescents, EtOH, Xylene	Yellow liquid	Air-drying	77	6,500	99	1 (23)
Boltorn® W3000	Emulsifying, soluble in alkyds, co-solvents, xylene	Yellow wax	Amphiphilic Air-drying	45 (fully aliphatic)	10,000	99	2.5 (35)



Precisely tailored
end-product properties





US005731095A

United States Patent [19]

Milco et al.

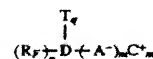
[11] Patent Number: **5,731,095**[45] Date of Patent: **Mar. 24, 1998**[54] **DENDRITIC POLYMER COATINGS**[75] Inventors: **Larry A. Milco; Donald A. Tomalia,**
both of Midland, Mich.[73] Assignee: **Oxazogen, Inc.,** Midland, Mich.[21] Appl. No.: **735,883**[22] Filed: **Oct. 23, 1996**[51] Int. Cl.⁶ **B32B 27/06; C08F 2/32;**
C08F 20/00[52] U.S. Cl. **428/482; 528/288; 528/290;**
528/299; 528/401; 525/437; 525/440; 525/540;
524/801; 524/802; 524/805; 524/839[58] Field of Search **528/288, 290,**
528/299, 401; 525/437, 440, 540; 524/801,
802, 805, 839; 428/482[56] **References Cited****U.S. PATENT DOCUMENTS**

4,460,029 7/1984 Schuetz et al. 152/359
 4,474,923 10/1984 Keskey et al. 524/458
 4,587,329 5/1986 Tomalia et al. 528/363
 5,418,301 5/1995 Hult et al. 525/437

Primary Examiner—Samuel A. Acquah

Attorney, Agent, or Firm—Price,Heneveld,Cooper,Dewitt &
Litton[57] **ABSTRACT**

A water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one terminal fluorocarbon moiety and at least one terminal anionic moiety, and which is suitable for use in preparing protective coating compositions is disclosed. The water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants are represented by the general formula:



where D represents a dendritic polymer, R_f represents a fluorocarbon containing moiety, A^- represents an anionic containing moiety, C^+ represents a cation, T represents a terminal group of the dendritic polymer which has not been functionalized with a fluorocarbon or anionic moiety, n and m are at least each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer. Also disclosed is a coating composition capable of forming a highly crosslinked, non-stick, protective coating. The coating composition includes a water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one terminal fluorocarbon moiety and at least one terminal anionic moiety, an oxazoline crosslinking agent, and a water-based solvent.

41 Claims, 1 Drawing Sheet

Major Macromolecular Architectures

I Linear	II Cross-Linked	III Branched	IV Dendritic
 Flexible Coil Rigid Rod Cyclic (Closed Linear) Polyrotaxane	 Lightly Cross-Linked Densely Cross-Linked Interpenetrating Networks	 Random Short Branches Random Long Branches Regular Comb-Branched Regular Star-Branched	(a) Random Hyperbranched (b) Controlled Hyperbranched (Comb-Burst™) (c) Regular Dendrons Dendrimers (Starburst)
1930's -	1940's -	1960's -	1980's -

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(KIM & WEBSTER, ET AL.)
(TOMALIA, ET AL. & GAUTHIER, ET AL.)
(TOMALIA, ET AL. & FRECHET, ET AL.)

Major Macromolecular Architectures

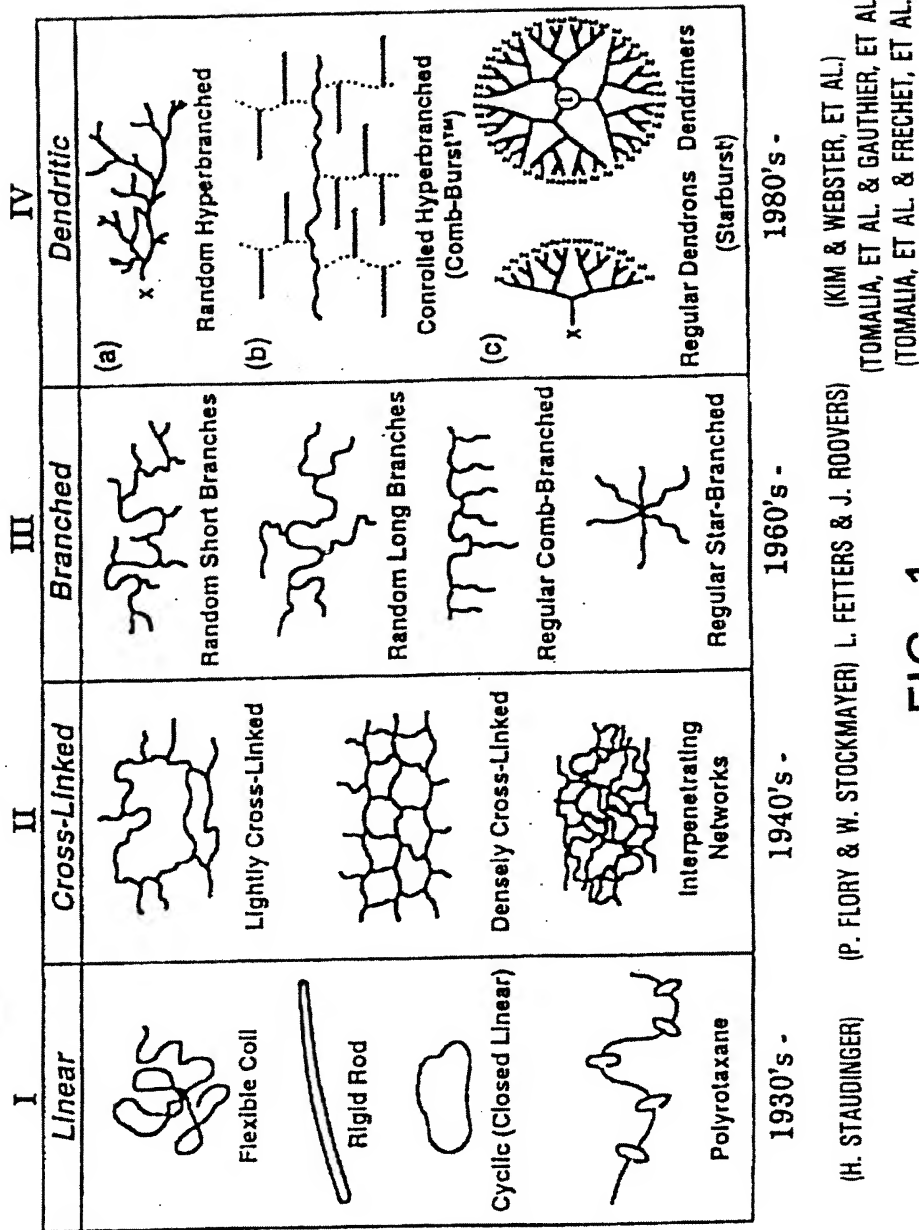


FIG. 1

DENDRITIC POLYMER COATINGS

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of Contract No. DAAH04-96-C-0024 awarded by Department Of The Army.

FIELD OF THE INVENTION

This invention relates to water-based non-stick coating compositions derived from water-soluble or water-dispersible dendritic polymer surfactants containing pendant fluorocarbon groups and pendant chemically reactive anionic moieties. Such surfactants can be thermally crosslinked at low temperatures with an oxazoline crosslinking agent to form low-energy coatings which exhibit excellent anti-stick properties.

BACKGROUND OF THE INVENTION

There is a considerable demand for thin film coatings to which other substances will not adhere. Coatings are required to protect surfaces from soils, stains, ice, graffiti, insects, oils, corrosion, and chemical and biological contaminants. Moreover, as legislative pressures to remove volatile organic compounds (VOCs) from coating formulations persist, the demand for alternative water-borne systems continues to increase.

Compounds and polymer coatings containing fluorocarbon groups have been widely used for providing non-stick properties to surfaces. The foremost commercially available non-stick coating is polytetrafluoroethylene (PTFE). PTFE is characterized by a low surface free energy, excellent thermal stability, low coefficient of friction, anti-wetting properties, electrical insulation properties, and chemical inertness. However, because of its insolubility in most solvents, PTFE is relatively difficult to apply and is not very easily processed. Notably, conventional thermoplastic techniques are not applicable to PTFE. Rather, the material is most commonly applied by high temperature sintering processes (up to 400° C.). Also, PTFE exhibits poor adhesion to many substrates and is susceptible to wear and soiling. PTFE forms coating surfaces having microscopic pores into which various adhesives and foulant materials can permeate and become mechanically locked. As a result, PTFE does not form an effective non-stick surface against many types of materials, including adhesive marine materials and other biological foulants.

Recently, non-stick coatings have been prepared by crosslinking linear perfluoroalkyl polymeric surfactants containing pendant ionic moieties such as carboxylate with poly(2-isopropenyl-2-oxazoline). These coatings have the advantage of being soluble in predominately aqueous solvents. The thermally cured coatings provide non-wettable, hard polymer surfaces which are only slowly attacked by common organic solvents. However, prolonged cure times (several hours) are required to achieve highly crosslinked (e.g., 80%) coatings with optimum physical/chemical properties. Moreover, the excessive cure times associated with these coatings preclude widespread commercial utility.

Consequently, it would be desirable to provide low VOC non-stick coating formulations which cure rapidly at low temperatures to afford highly crosslinked non-stick coatings possessing excellent release properties.

SUMMARY

The present invention pertains to a water-soluble or water-dispersible fluorine-containing dendritic polymer sur-

factant having at least one pendant fluorocarbon moiety and at least one pendant anionic moiety.

This invention also pertains to coating compositions comprising an aqueous solvent, a water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one pendant fluorocarbon moiety and at least one pendant anionic moiety, and a water-soluble or water-dispersible crosslinking agent having a plurality of oxazoline moieties which are capable of reacting with the anionic moiety of the dendritic polymer surfactant to form a crosslinked polymeric coating.

The non-stick coating compositions of this invention can be easily applied, such as with a brush, roller, spray gun, etc., and rapidly cured at a low temperature. Further, because the fluorine-containing dendritic polymer surfactants and coating compositions of this invention are water-soluble or water-dispersible, they can be formulated with low amounts of volatile organic solvents, whereby ease of application and rapid curing to form a hard, very low-porosity, non-stick coating is achieved while minimizing environmental and health hazards.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of the major macromolecular architectures.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The dendritic polymers which may be used in the practice of this invention include generally any of the known dendritic architectures including dendrimers, regular dendrons, controlled hyperbranched polymers, dendrigrafts, and random hyperbranched polymers. Dendritic polymers are polymers with densely branched structures having a large number of reactive groups. A dendritic polymer includes several layers or generations of repeating units which all contain one or more branch points. Dendritic polymers, including dendrimers and hyperbranched polymers, are prepared by condensation reactions of monomeric units having at least two different types of reactive groups. This fourth major class of polymer architecture is shown in FIG. 1.

Dendrimers are comprised of a plurality of dendrons that emanate from a common core which can be a single atom or a group of atoms. Each dendron generally consists of terminal surface groups, interior branch junctures having branching functionalities greater than or equal to two, and divalent connectors that covalently connect neighboring branching junctures. Dendrons and dendrimers can be prepared by convergent or divergent synthesis. Divergent synthesis of dendrons and dendrimers involves a molecular growth process which occurs through a consecutive series of geometrically progressive step-wise additions of branches upon branches in a radially outward molecular direction to produce an ordered arrangement of layered branch cells, in which each macromolecular includes a core cell, one or more layers of internal cells, and an outer layer of surface cells, wherein each of the cells includes a single branch juncture. The cells can be the same or different in chemical structure and branching functionality. The surface branch cells may contain either chemically reactive or passive functional groups. Chemically reactive surface groups can be used for further extension of dendritic growth or for modification of dendritic molecular surfaces. The chemically passive groups may be used to physically modify dendritic surfaces, such as to adjust the ratio of hydrophobic to hydrophilic terminals. Convergent synthesis of dendrim-

ers and dendrons involves a growth process which begins from what will become the surface of the dendron or dendrimer and progresses radially in a molecular direction toward a focal point or cove.

Dendrons and dendrimers may be ideal or non-ideal, i.e., imperfect or defective. Imperfections are normally a consequence of either incomplete chemical reactions, or unavoidable competing side reactions. In practice, real dendritic polymers are generally non-ideal, i.e., contain certain amounts of structural imperfections.

A third method by which dendrimers and dendrons can be prepared is by using a one-pot synthesis in which dendritic polymers are prepared by a step-growth polymerization reaction of a single type of monomer having a single reactive group of a first type (B) and a plurality (y) of reactive groups of a second type (A), i.e., a B-A_y type monomer, which is initiated by a core having a plurality (x) of the A type reactive groups, wherein A groups can react with B groups, but not with other A groups, and B groups cannot react with other B groups. The one-pot synthesis method is simpler and less expensive than the divergent and convergent synthesis methods. However, the one-pot synthesis method lacks reaction control, which leads to more polydispersed products with larger deviations from ideal dendron structure.

Hyperbranched polymers represent a class of dendritic polymers which contain high levels of non-ideal irregular branching arrays as compared with the more nearly perfect regular structure of dendrons and dendrimers. Specifically, hyperbranched polymers contain a relatively high number of irregular branching arrays in which not every repeat unit contains a branch juncture. Consequently, hyperbranched polymers may be viewed as intermediate between randomly branched polymers and regular dendrons and dendrimers, yet dendritic, because of their relatively high branch-juncture content per individual macromolecule.

The preparation and characterization of dendrimers, dendrons, random hyperbranched polymers, controlled hyperbranched polymers, and dendrigrafts is well known. Examples of dendrimers and dendrons, and methods of synthesizing the same are set forth in U.S. Pat. Nos. 4,507,466; 4,558,120; 4,568,737; 4,587,329; 4,631,337; 4,694,064; 4,713,975; 4,737,550; 4,871,779 and 4,857,599. Examples of hyperbranched polymers and methods of preparing the same are set forth, for example, in U.S. Pat. No. 5,418,301.

More generally dendritic polymers or macromolecules are characterized by a relatively high degree of branching (DB), which is defined as the number average fraction of branching groups per molecule, i.e., the ratio of terminal groups plus branch groups to the total number of terminal groups, branch groups and linear groups. For ideal dendrons and dendrimers the degree of branching is one. For linear polymers the degree of branching is zero. Hyperbranched polymers have a degree of branching which is intermediate between that of linear polymers and ideal dendrimers. The dendritic polymers used in this invention desirably have a degree of branching which is at least equal to or greater than 0.1, more preferably greater than or equal to 0.4, and most preferably greater than 0.5.

Dendritic polymers suitable for use with the invention also include macromolecules commonly referred to as cascade molecules, arborols, arborescent grafted molecules, and the like. Suitable dendritic polymers also include bridged dendritic polymers (i.e., dendritic macromolecules linked together either through surface functional groups or through a linking molecule connecting surface functional

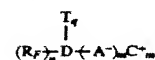
groups together) and dendritic polymer aggregates. The dendritic polymer used in the practice of this invention can be generationally monodisperse or generationally polydisperse solutions. Dendritic polymers in a monodisperse solution are substantially all of the same generation, and hence of uniform size and shape. The dendritic polymers in the polydisperse solution comprise a distribution of different generation polymers. Furthermore, the dendritic polymer molecules may be mixtures of different interior and exterior composition or functionality.

Generally, any of the known dendritic polymers having anionic terminal groups, or having terminal groups which can be reacted with another compound to provide anionic terminal groups, are suitable for use in preparing the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants and coating compositions of this invention. Examples of suitable dendritic polymers include poly(ether) dendrons, dendrimers and hyperbranched polymers, poly(ester) dendrons, dendrimers and hyperbranched polymers, poly(thioether) dendrons, dendrimers and hyperbranched polymers, poly(arylalkylene) dendritic polymers, etc.

While generally any dendritic polymer can be used in the preparation of the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants of this invention, it is desirable to avoid the use of dendritic polymers which are at least as basic as the oxazoline moieties of the crosslinking agent in the coating compositions of this invention because they tend to inhibit proton transfer to the oxazoline functional moieties and consequently inhibit crosslinking. Examples of dendritic polymers which tend to inhibit protonation of the oxazoline moieties include generally any of the amine containing dendrimers, such as the polyamidoamine (PAMAM) dendritic polymers.

The terminal or surface reactive groups of the dendritic polymers which are used to prepare the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants used in the preparation of non-stick coatings in accordance with this invention include any nucleophilic or electrophilic group which is capable of forming covalent bonds with a fluorine-containing compound and an anionic moiety-containing compound to afford a dendritic polymer surfactant.

The water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants suitable for preparing the non-stick coatings of this invention are represented by the general formula



where D represents a dendritic polymer, R_f represents a fluorocarbon-containing moiety, A⁻ represents an anionic containing moiety, C⁺ represents a cation, T represents a terminal group which has not been functionalized with a fluorocarbon or anionic moiety, n and m are each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer.

Hydroxy-terminated hyperbranched polyesters are presently preferred starting materials for the preparation of water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants in accordance with the invention because of their relatively low cost and commercial availability. Suitable hydroxy-terminated hyperbranched polyesters for use in the manner of this invention include first through fourth generation polymers having molecular

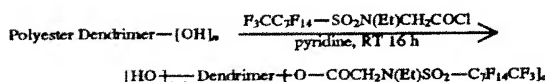
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weights ranging from about 1,500 to about 8,000, and having from about 16 to about 64 terminal hydroxy groups.

The fluorine-containing dendritic polymer surfactants which are employed in the coating compositions of this invention are provided with at least one pendent fluorocar-

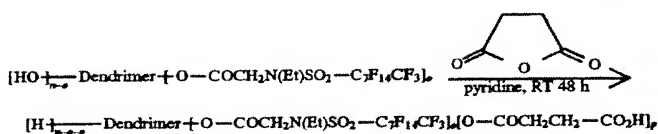
bon moiety and at least one pendent anionic moiety. The fluorocarbon moiety is a linear or branched fluoroalkyl group having at least one terminal trifluoromethyl group and containing at least three fully fluorinated carbon atoms. Preferred fluoroalkyl moieties are fully fluorinated alkyls, i.e., perfluoroalkyls.

Fluorocarbon moieties can be introduced into a dendritic polymer by reacting the dendritic polymer with a fluorine-containing compound having a fluoroalkyl moiety and a reactive linking moiety capable of covalently bonding to the reactive terminal groups of the dendritic polymer. For example, a hydroxy-terminated hyperbranched polyester can be reacted with a fluorine-containing acyl halide in the presence of a suitable solvent, such as pyridine, for a suitable period of time (e.g., 16 hours) at room temperature to form a perfluoroalkyl-terminated hyperbranched polyester as follows:



where n is the total number of terminal groups on the dendritic polymer and O is the number of fluoroalkyl-containing terminal moieties.

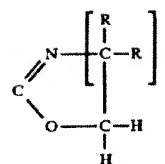
Preferred anionic moieties include carboxylate groups and thiol groups, with carboxylate terminal moieties being most preferred. Anionic moieties can be covalently bonded to the reactive terminals of the dendritic polymer by reacting a anionic moiety-containing compound or a compound capable of forming an anionic moiety with the reactive terminal groups of the dendritic polymer. For example, terminal carboxyl moieties can be introduced into a hydroxy-terminated dendritic polymer by reacting the terminal hydroxy groups with an anhydride of a dicarboxylic acid. For instance, the above perfluoroalkyl-terminated hyperbranched polyester can be reacted with succinic anhydride at room temperature for a suitable period of time (e.g., 48 hours) in a suitable solvent (e.g., pyridine) to form a carboxyl/perfluoroalkyl-terminated hyperbranched polyester as follows:



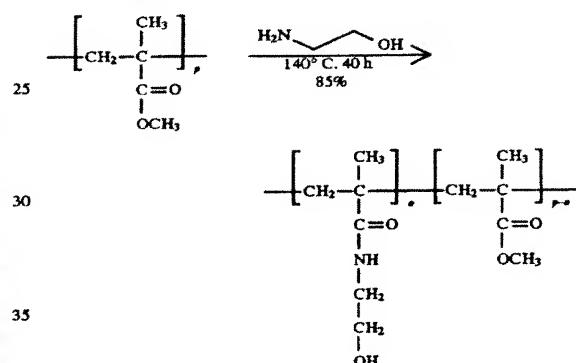
The number of anionic terminal moieties and perfluoroalkyl terminal moieties can be varied as desired to provide custom tailored properties for particular applications. In general, higher levels of anionic terminal moieties provide better water-solubility or water-dispersibility.

The crosslinking compounds used in the preparation of coating compositions in accordance with this invention are compounds containing a plurality (at least two) of oxazoline moieties represented by the formula

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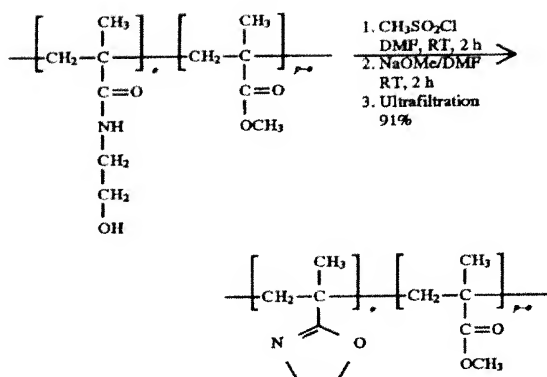


where each R is a hydrogen atom, a hydroxy methyl group or an organic radical, and k is 1 or 2, most preferably 1. Preferred oxazoline crosslinking agents include polymeric compounds containing pendant oxazolines moieties, such as poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate), poly(IPO/MMA). For example, suitable polymeric oxazoline crosslinking agents can be prepared by reacting a polyacrylate, such as poly(methyl methacrylate), with ethanolamine, e.g., at 140°C . for 40 hours in an aminolysis reaction, to produce an acrylic polymer having pendant hydroxy groups as follows:



where P is the total number of acrylate units or monomers in the polyacrylate and o is the number of acrylate units which have been reacted. The above amidated polyacrylate is subsequently subjected to conditions which cause the pendant hydroxyethylamide moieties to undergo ring formation to form oxazoline moieties. For example, in the presence of $\text{CH}_3\text{SO}_2\text{Cl}$ in a suitable solvent, such as DMF, the pendant hydroxyethylamide groups are converted into oxazoline moieties at room temperature in about 2 hours to

form an acrylic polymer having pendant oxazoline moieties as follows:



Coating formulations in accordance with the invention are prepared by combining the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants and oxazoline crosslinking agents in water or in an aqueous solution comprised primarily of water and containing a minor amount of an organic solvent. Organic cosolvents are generally not preferred, although small amounts, i.e., 20 percent by weight or less, may be added to aid curing.

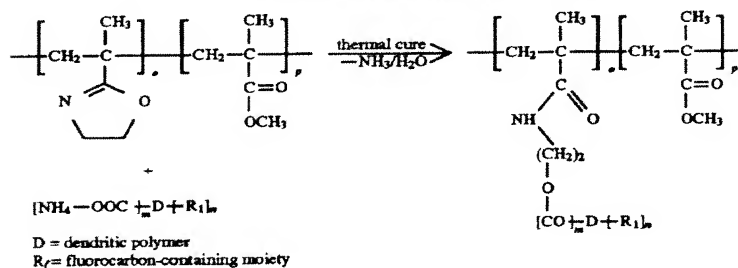
The coating compositions of this invention can be applied by generally any conventional method, such as those used to apply paint to surfaces. Suitable techniques for applying the coatings of this invention include wiping, brushing, spraying, dipping, and spin-coating. Suitable substrates for the coatings of this invention include metal, plastic, glass, masonry, paper and textiles. Any suitable heating method may be used to cure the coatings, such as radiant heating and heated air.

The coating compositions of this invention are extremely stable, i.e., crosslinking does not occur to any appreciable extent during storage of the coating compositions in a sealed container.

After application, the coating compositions of this invention cure very rapidly at relatively low temperatures, e.g., typically over 80% cure in 15 minutes or less at a temperature of 110° C. The coating compositions of the invention also have the advantage of being non-flammable, and have very low or no volatile organic compounds (VOCs).

Curing of the coating compositions of this invention occurs upon application of heat by reaction of the oxazoline moieties of the crosslinking agent with the anionic groups of the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant. For example:

PREPARATION OF WATER-BORNE NON-STICK COATINGS:
CROSSLINKING REACTION



Examples of suitable cosolvents include ethylene glycol, propylene glycol, and the like. The concentrations of the formulation can typically range from about 0.01 to about 60 weight percent solids (i.e., the dendritic polymer surfactant and oxazoline crosslinker constitute from about 0.01 to about 60% of the composition by weight) and more preferably from about 1.0 to about 25 weight percent solids (i.e., from 1 to 25 weight percent dendritic polymer surfactant and oxazoline crosslinker). The preferred concentrations will depend on such factors as the desired viscosity, coating thickness and method of application. The amounts of water-dispersible or water-soluble fluorine-containing dendritic polymers and oxazoline crosslinking agents are selected so that the mole ratio of oxazoline moieties to anionic moieties is preferably about 1:1, for example, from about 0.8:1 to about 1.2:1. Lower or higher ratios provide coatings with more hydrophilic surfaces. The pH of the aqueous formulation is preferably kept slightly basic to avoid acid catalyzed hydrolysis of the oxazoline groups in the crosslinking agent. The pH of the formulation is preferably adjusted to a range of from about 7 to about 8. However, the preferred pH will depend on the pH stabilities of other functional groups present in the polyoxazoline and fluorine-containing dendritic polymer surfactant. The preferred cation, C⁺, include ammonium and low molecular weight protonated amines.

EXAMPLE 1

Preparation of Carboxy/Perfluoroalkyl-Terminated Hyperbranched Polymers

Perstorp polyol and pyridine were combined in a 100 ml round bottom flask under nitrogen. The mixture became homogeneous after stirring at room temperature for 2 hours. To the vigorously stirred mixture was added a solution of C₈F₁₇SO₂N(Et)CH₂COCl in dry acetone (38% w/w) at a rate of 0.5 ml/minute using a syringe pump. The mixture was then stirred overnight at room temperature. Succinic anhydride was added to the solution in a single portion. After 48–72 hours, the reaction mixture was diluted with methanol (150 ml) and purified by ultrafiltration employing a tangential flow device (Amicon) equipped with a MWco=1000 membrane (Amicon YM1). After 8 retentate volumes of permeate were obtained, the retentate was concentrated under reduced pressure using a rotary evaporator. The residue was evacuated under high vacuum at room temperature to afford a viscous liquid. The mole percent of terminal carboxyl groups and terminal perfluoroalkyl groups were determined from the ¹HNMR spectrum of the product (300 MHz, acetone-d₆/TMS). The mole percent of terminal carboxy groups was determined from the ratio of the integrated

intensities of the signals at δ 2.6 (br s, $\text{COCH}_2\text{CH}_2\text{CO}$) and δ 3.5–3.7 (complex, CH_2OH). The mole percent of terminal perfluoroalkyl groups was determined from the ratio of integrated intensities of the signals at δ 2.6 (br s, $\text{COCH}_2\text{CH}_2\text{CO}$) and δ 4.2–4.4 (complex, $\text{CH}_2\text{O—CO}$ and N—CH_2).

Products derived from generation 2, 3, and 4 hyperbranched polyesters were prepared using the quantities of reagents specified in Table 1.

EXAMPLE 2

Preparation of poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate)

A 5 liter 3-neck round bottom flask was equipped with a reflux condenser, mechanical stirrer (teflon blade), and a thermometer attached to a Therm-o-Watch temperature controller. To the flask was added poly(methyl methacrylate) (MW=75,000, 500 g, 5 moles ester) and ethanolamine (2443 g, 40 moles) under nitrogen. The mixture was stirred and heated at 150° C. for 35 hours and then allowed to cool to room temperature. The mixture was diluted with methanol (5 liters) and added dropwise to 3 volumes of mechanically stirred toluene. After completion of the addition, the mixture was allowed to stand undisturbed for 10 minutes. The supernatant liquid was decanted and the residue was washed twice with toluene (2×300 mL). The residue was dissolved in methanol (3 liters) and added dropwise to three times the volume of stirred toluene. The precipitate was collected in a Buchner funnel and washed twice with toluene (2×200 mL). Drying overnight under high vacuum at 50° C. afforded poly(2-hydroxyethylmethacrylamide-co-methyl methacrylate) (550 g, 85%).

To a 1 liter 3 neck round bottom flask equipped with a mechanical stirrer was added poly(2-hydroxyethylmethacrylamide-co-methyl methacrylate) (52 g, 403 mmole OH) and dimethylformamide (DMF, 300 mL) under nitrogen. The stirred mixture was heated at 150° C. until complete dissolution occurred and then allowed to cool to room temperature. The stirred mixture was treated with methanesulfonyl chloride (58 g, 506 mmole) and heated at 100° C. until homogeneous. The mixture was then stirred an additional 2 hours at room temperature. The mixture was diluted with DMF (50 mL) and added during a 10 minute period to a solution of sodium methoxide (101 g, 1.87 mole) in DMF (100 mL) under nitrogen. After stirring for 2 hours at room temperature, most of the solvent was removed by vacuum distillation (1–5 mmHg, 80°–150° C). The resulting residue was dissolved in methanol (3 liters) and ultrafiltered using a tangential ultrafiltration system (Amicon B6) equipped with regenerated cellulose membrane (MWCO=3000, 4.2 ft²). After 8 retentate volumes of permeate were collected, the retentate was filtered through Whatman No.1 paper. The filtrate was concentrated under reduced pressure using a rotary evaporator. The residue was evacuated at high vacuum for 18 hours to afford the desired product (41 g, 91%) as a slightly brown solid. The mole percentage of oxazoline was determined to be 86%, based on the integrated intensities of the oxazoline CH_2 (multiplets, δ 3.77 and 4.28, 4H) and ester CH_3 (s, δ 3.63, 3H) signals in the ¹H NMR spectrum (300 MHz, $\text{CD}_3\text{OD/TMS}$) of the product.

EXAMPLE 3

Formulation of Coatings

The carboxy/perfluoroalkyl-terminated hyperbranched polyester was dissolved in isopropanol (30% w/w). The pH

of the solution was adjusted to 7–8 with ammonium hydroxide (1N). To the solution was added an aqueous solution of polyIPO/MMA (10% w/w, 7.85 mmoles oxazoline/g polymer) in an amount required to achieve a 1:1 mole ratio of oxazoline/ CO_2H . Ethylene glycol was added to the mixture in an amount equal to the combined weight of hyperbranched polymer and polyIPO/MMA. The mixture was then diluted with deionized water to achieve a final concentration of 10–12% w/w solids. The mixture was stirred until homogeneous and then filtered (0.5 μm).

EXAMPLE 4

Application of Coatings to Substrates

Each coating formulation was applied to a single infrared AgCl crystal window (2.5×2.5×0.1 cm) and a glass microscope slide (25×75×1 mm) with a Paul-Gardner wire-wound film applicator (AP-FD02.5, wire #2.5) for determination of the extent of crosslinking and contact angle measurements, respectively.

EXAMPLE 5

Thermal Cure of Coatings

Freshly coated substrates were cured in an oven at 110° C. The infrared windows were removed from the oven following cumulative cure times of 0.25 h, 0.5 h, 0.75 h, 1 h, 4 h, 10 h, 24 h, and 46 h (or 48 h). The windows were allowed to cool to room temperature prior to spectrometric analysis. The coated glass slides were removed from the oven after 1 hour of cure and allowed to cool to room temperature prior to contact angle measurements.

EXAMPLE 6

Determination of the Extent of Crosslinking in Coatings

The extent of crosslinking in the coatings was determined by monitoring the amide N—H, amide C=O, and oxazoline C=N stretching absorptions using FTIR spectrometry. Spectra were recorded on a Nicolet FTIR spectrometer and analyzed using OMNIC FTIR software. FTIR spectra of the cured films feature an amide N—H stretching absorption in the region from 1500 to 1550 cm^{-1} and overlapping amide C=O and oxazoline C=N stretching absorptions in the region from 1580 to 1680 cm^{-1} . The extent of crosslinking in cured coatings was calculated using equation 1:

Extent of crosslinking, % = (1)

$$\frac{A_{\text{amide N-H}} \cdot A_{\text{amide C=O}} - A_{\text{amide C=O}} \cdot A_{\text{oxazoline C=N}}}{A_{\text{amide C=O}} \cdot A_{\text{oxazoline C=N}}} \times 100$$

here $A_{\text{amide N-H}}$ is the integrated amide N—H absorbance, $A_{\text{amide C=O}}$ is the integrated amide C=O absorbance, $A_{\text{oxazoline C=N}}$ is the integrated oxazoline C=N absorbance, $A_{\text{amide N-H}}$ is the absorptivity of the amide N—H stretching absorption.

$A_{\text{amide C=O}}$ is the absorptivity of the amide C=O stretching absorption, and $A_{\text{oxazoline C=N}}$ is the absorptivity of the oxazoline C=N stretching absorption. Absorptivities for the amide N—H, amide C=O, and oxazoline C=N stretching absorptions were derived from the slopes of absorbance versus concentration plots for the model compounds poly [N-(2-hydroxyethyl)methacrylamide-co-methyl methacrylate], N-(2-hydroxyethyl)-2,2-

dimethylpropanamide, and poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate), respectively. The absorptivity of the amide N—H stretching absorption is 8×10^6 cm/mole in the range from 1500–1550 cm^{-1} . The absorptivities of the amide C=O and oxazoline C=N stretching absorptions are 1.81×10^7 cm/mole and 1.58×10^7 cm/mole in the range from 1580–1680 cm^{-1} .

The results of cure studies employing hyperbranched polymer coatings are shown in Table 2.

EXAMPLE 7

Contact Angle Measurements

The contact angles of deionized water and hexadecane (Aldrich, 90+%) on cured coatings were determined using a Rame-Hart goniometer (Model A-100). The liquid drops were applied using a microliter syringe (Gilmont). The advancing contact angle of water was measured on a 50 μl water droplet and the receding contact angle was measured after 30 μl of water was withdrawn from the droplet. The advancing contact angle of hexadecane was measured on a 5 μl droplet and the receding contact angle was measured following the withdrawal of 3 μl of hexadecane from the droplet.

The results of contact angle measurements performed on hyperbranched polymer coatings are provided in Table 3.

TABLE 2-continued

Curing of Hyperbranched Polymer Coatings†						
Hyperbranched Polymer Surfactant						
Coat- ing	Gene- ration	mole % R_f	mole % CO_2H	Cure Time hours	Crosslinking %	
3	3	6.4	46	0.25	82	
				0.5	88	
				0.75	88	
				1	89	
				2	91	
4	3	40	31	4	94	
				10	99	
				24	100	
				48	99	
				0.25	86	
				0.5	91	
				0.75	94	
				1	96	
				2	97	
				4	100	
5	4	5.1	63	10	99	
				24	98	
				46	97	
				0.25	76	
				0.5	79	
				0.75	81	

TABLE 1

Preparation of Carboxy/Perfluoroalkyl-Terminated Hyperbranched Polymers										
Hyperbranched Polymer				$\text{C}_6\text{H}_4\text{SO}_2\text{N}(\text{Et})\text{CH}_2\text{COCl}$		Succinic Anhydride		Pyridine	Product Composition	
Preparation	Generation	grams	mmoles OH	grams	mmoles	grams	mmoles	ml	mole % R_f	mole % CO_2H
1	2	1.90	17.1	0.85	1.40	3.10	30.0	14.0	12	56
2	2	1.30	11.7	2.17	3.60	1.50	15.0	10.0	22	36
3	3	2.82	24.7	1.21	2.00	2.50	25.0	25.0	6.4	46
4	3	3.16	27.7	8.80	14.6	2.80	28.0	28.0	40	31
5	4	3.00	26.0	1.28	2.12	3.00	30.0	25.0	5.1	63
6	4	3.00	26.0	4.83	8.00	3.00	30.0	25.0	25.0	48

$R_f = -\text{C}_8\text{F}_{17}$

TABLE 2

Curing of Hyperbranched Polymer Coatings†						
Hyperbranched Polymer Surfactant						
Coat- ing	Gene- ration	mole % R_f	mole % CO_2H	Cure Time hours	Crosslinking %	
1	2	12	56	0.25	83	
				0.5	88	
				0.75	89	
				1	90	
				2	93	
				4	94	
				10	96	
				24	97	
				46	99	
				0.25	81	
2	2	22	36	0.5	89	
				0.75	91	
				1	93	
				2	97	
				4	100	
				10	100	
				24	95	
				46	97	

TABLE 2-continued

Curing of Hyperbranched Polymer Coatings†						
Hyperbranched Polymer Surfactant						
Coat- ing	Gene- ration	mole % R_f	mole % CO_2H	Cure Time hours	Crosslinking %	
6	4	25	48	1	82	
				2	86	
				4	87	
				10	91	
				24	95	
				48	97	
				0.25	82.2	
				0.5	87	
				0.75	88	
				1	91	
65				2	93	
				4	96	
				10	97	
				24	99.6	
				48	100	

Coatings cured at 110° C.
 $R_f = -\text{C}_8\text{F}_{17}$

TABLE 3

Physical Properties of Hyperbranched Polymer Coatings†							
Hyperbranched Polymer Surfactant				Contact Angle, degrees			
Coating	Generation	mole % R _f	mole % CO ₂ H	Θ _h water	Θ _f water	Θ _h hexadecane	Θ _f hexadecane
1	2	12	56	112	85	61	61
2	2	22	36	111	84	66	65
3	3	6.4	46	112	81	66	66
4	3	40	31	115	89	68	67
5	4	5.1	63	115	88	68	67
6	4	25	48	106	79	68	65

†Coatings cured at 110° C. for 1 hour
R_f = —C₈F₁₇,

It will be apparent to those skilled in the art that various modifications to the preferred embodiment of the invention as described herein can be made without departing from the spirit or scope of the invention as defined by the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one pendant fluorocarbon moiety and at least one pendant anionic moiety.

2. The dendritic polymer surfactant of claim 1 represented by the formula



where D represents a dendritic polymer, R_f represents a fluorocarbon-containing moiety, A[−] represents an anionic-containing moiety, C⁺ represents a cation, T represents a terminal group of the dendritic polymer which has not been functionalized with a fluorocarbon or anionic moiety, n and m are each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer.

3. The dendritic polymer surfactant of claim 2, wherein the dendritic polymer is a dendron or dendrimer.

4. The dendritic polymer surfactant of claim 2, wherein the dendritic polymer is a hyperbranched polyester.

5. The dendritic polymer surfactant of claim 2, wherein the fluorocarbon-containing moiety includes a linear or branched fluoroalkyl group having at least one terminal trifluoromethyl group and containing at least three fully fluorinated carbon atoms.

6. The dendritic polymer surfactant of claim 2, wherein the fluorocarbon-containing moiety includes a perfluoroalkyl group.

7. The dendritic polymer surfactant of claim 2, wherein the fluorocarbon-containing moiety is represented by the formula —COCH₂N(C₂H₅)SO₂(C₇F₁₄CF₃).

8. The dendritic polymer surfactant of claim 2, wherein the anionic-containing moiety includes a carboxylate group.

9. The dendritic polymer surfactant of claim 2, wherein the T groups are hydroxy groups.

10. The dendritic polymer surfactant of claim 2, wherein the cation is ammonium.

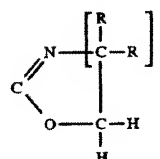
11. The dendritic polymer surfactant of claim 2, wherein the cation is a low molecular weight protonated amine.

12. A non-stick coating composition comprising:

a water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one pen-

dant fluorocarbon moiety and at least one pendant anionic moiety;

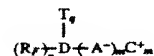
a crosslinking compound containing a plurality of oxazoline or oxazine moieties represented by the formula



where each R is a hydrogen atom, a hydroxy methyl group or an organic radical, and k is one or two; and

an aqueous solvent comprising primarily water and optionally containing a minor amount of an organic solvent.

13. The coating composition of claim 12, wherein the dendritic polymer surfactant is represented by the formula



where D represents a dendritic polymer, R_f represents a fluorocarbon containing moiety, A[−] represents an anionic-containing moiety, C⁺ represents a cation, T represents a terminal group of the dendritic polymer which has not been functionalized with a fluorocarbon or anionic moiety, n and m are each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer.

14. The coating composition of claim 13, wherein the T groups are hydroxy groups.

15. The coating composition of claim 13, wherein the dendritic polymer is a hyperbranched polyester.

16. The coating composition of claim 13, wherein the fluorocarbon moiety is a linear or branched fluoroalkyl group having at least one terminal trifluoromethyl group and containing at least three fully fluorinated carbon atoms.

17. The coating composition of claim 16, wherein the anionic-containing moiety includes a carboxylate group.

18. The coating composition of claim 13, wherein the oxazoline crosslinking agents include polymeric compounds containing pendant oxazoline moieties.

19. The coating composition of claim 18, wherein the oxazoline crosslinking agent is an acrylate polymer having pendant oxazoline moieties.

20. The coating composition of claim 13, wherein the dendritic polymer surfactant and oxazoline crosslinking agent comprise from about 0.01 to about 60% of the composition by weight.

15

21. The coating composition of claim 20, wherein the amounts of fluorine-containing dendritic polymers and oxazoline crosslinking agents are selected so that the mole ratio of oxazoline moieties to anionic moieties is from about 0.8:1 to about 1.2:1.

22. The coating composition of claim 13, wherein the pH is from about 7 to about 8.

23. The coating composition of claim 13, wherein the fluorocarbon-containing moiety includes a perfluoroalkyl group.

24. The coating composition of claim 13, wherein the fluorocarbon-containing moiety is represented by the formula—COCH₂N(C₂H₅)SO₂(C₇F₁₄CF₃).

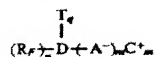
25. The coating composition of claim 13, wherein the anionic-containing moiety includes a carboxylate group.

26. The coating composition of claim 13, wherein the cation is ammonium.

27. The coating composition of claim 13, wherein the cation is a low molecular weight protonated amine.

28. A highly crosslinked protective coating comprising a reaction product of a dendritic polymer surfactant having at least one pendant fluorocarbon moiety and at least one pendant anionic moiety and an oxazoline crosslinking agent.

29. The coating of claim 28, wherein the dendritic polymer surfactant is represented by the formula



where D represents a dendritic polymer, R_f represents a fluorocarbon containing moiety, A⁻ represents an anionic-containing moiety, C⁺ represents a cation, T represents a terminal group of the dendritic polymer which has not been functionalized with a fluorocarbon or anionic moiety, n and m are each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer.

16

30. The coating of claim 29, wherein the T groups are hydroxy groups.

31. The coating of claim 29, wherein the dendritic polymer is a hyperbranched polyester.

32. The coating of claim 29, wherein the fluorocarbon moiety is a linear or branched fluoroalkyl group having at least one terminal trifluoromethyl group and containing at least three fully fluorinated carbon atoms.

33. The coating of claim 31, wherein the anionic-containing moiety includes a carboxylate group.

34. The coating of claim 29, wherein the oxazoline crosslinking agents include polymeric compounds containing pendant oxazoline moieties.

35. The coating of claim 34, wherein the oxazoline crosslinking agent is an acrylate polymer having pendant oxazoline moieties.

36. The coating of claim 35, wherein the amounts of fluorine-containing dendritic polymers and oxazoline crosslinking agents are selected so that the mole ratio of oxazoline moieties to anionic moieties is from about 0.8:1 to about 1.2:1.

37. The coating of claim 29, wherein the fluorocarbon-containing moiety includes a perfluoroalkyl group.

38. The coating of claim 29, wherein the fluorocarbon-containing moiety is represented by the formula—COCH₂N(C₂H₅)SO₂(C₇F₁₄CF₃).

39. The coating of claim 29, wherein the anionic-containing moiety includes a carboxylate group.

40. The coating of claim 29, wherein the cation is ammonium.

41. The coating of claim 29, wherein the cation is a low molecular weight protonated amine.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,731,095

DATED : March 24, 1998

INVENTOR(S) : Larry A. Milco and Donald A. Tomalia

Page 1 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Abstract, line 15;

Delete "at least" (1st occurrence).

Column 2, line 56;

"macromolecular" should be ~~macromolecule~~.

Column 3, line 4;

"cove" should be ~~core~~.

*Column 5, line 36;

"a" (1st occurrence) should be ~~an~~.

Column 5, After line 55, (2nd equation);

$[H]_{nop}$ Dendrimer (etc.)" should be

$-[HO]_{nop}$ Dendrimer (etc.)~~.~~

Column 6, line 13

"oxazolines" should be ~~oxazoline~~.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,731,095

DATED : March 24, 1998

INVENTOR(S) : Larry A. Milco and Donald A. Tomalia

Page 2 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Columns 11 & 12, Table 2, line 2 of the 3 Sections, Subheadings;

"Hyperbranced" should be ~~-Hyperbranched-~~.

Column 16, claim 32, line 7;

"trifluoromethyl" should be ~~-trifluoromethyl-~~.

Signed and Sealed this
First Day of September, 1998

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks



US005418301A

United States Patent [19]

Hult et al.

[11] Patent Number: 5,418,301

[45] Date of Patent: May 23, 1995

[54] DENDRITIC MACROMOLECULE AND
PROCESS FOR PREPARATION THEREOF[75] Inventors: Anders Hult, Täby; Eva Malmstrom,
Bandhagen; Mats Johansson,
Stockholm; Kent Sörensen, Perstorp,
all of Sweden

[73] Assignee: Perstorp AB, Perstorp, Sweden

[21] Appl. No.: 256,493

[22] PCT Filed: Feb. 24, 1993

[86] PCT No.: PCT/SE93/00148

§ 371 Date: Jul. 13, 1994

§ 102(e) Date: Jul. 13, 1994

[87] PCT Pub. No.: WO93/17060

PCT Pub. Date: Sep. 2, 1993

[30] Foreign Application Priority Data

Feb. 26, 1992 [SE] Sweden 9200564

[51] Int. Cl.⁶ C08F 20/00[52] U.S. Cl. 525/437; 528/271;
528/274; 528/279; 528/281; 528/282; 528/283;
528/295.5; 528/300; 528/301; 528/303;
528/306; 525/438; 525/440; 525/442; 525/444;
525/444.5; 525/445; 525/449; 525/450[58] Field of Search 528/271, 274, 279, 281,
528/282, 283, 295.5, 300, 301, 303, 306;
525/437, 438, 440, 442, 444, 444.5, 445, 450,
449

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Molecular-Level Control of Size, Shape, Surface
Chemistry, Topology, and Flexibility from Atoms to
Macroscopic Matter", *Angew. Chem. Int. Ed. Engl.*
29:138-175.

Primary Examiner—Samuel A. Acquah

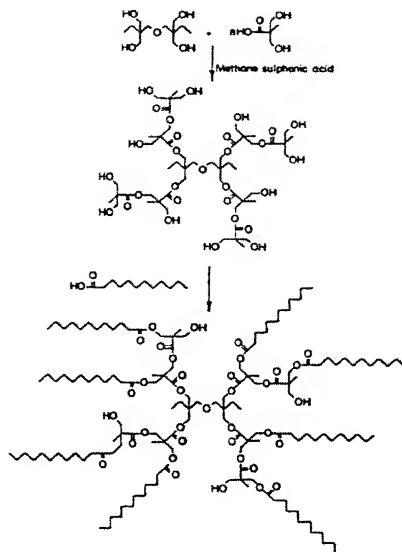
Attorney, Agent, or Firm—Scully, Scott, Murphy &
Presser

[57]

ABSTRACT

The invention relates to a dendritic macromolecule of the polyester type comprising a central initiator molecule or initiator polymer having one or more reactive hydroxyl groups (A). The groups (A) are under formation of an initial tree structure bonded to reactive carboxyl groups (B) of a monomeric chain extender having the two reactive groups (A) and (B). The tree structure is optionally extended and further branched from the initiator molecule or initiator polymer by addition of further molecules of a monomeric chain extender by means of bonding between the reactive groups (A) and (B) thereof and is thereafter optionally further extended by reaction with a chain stopper. The invention also comprises a process for preparation of the dendritic macromolecule.

25 Claims, 2 Drawing Sheets



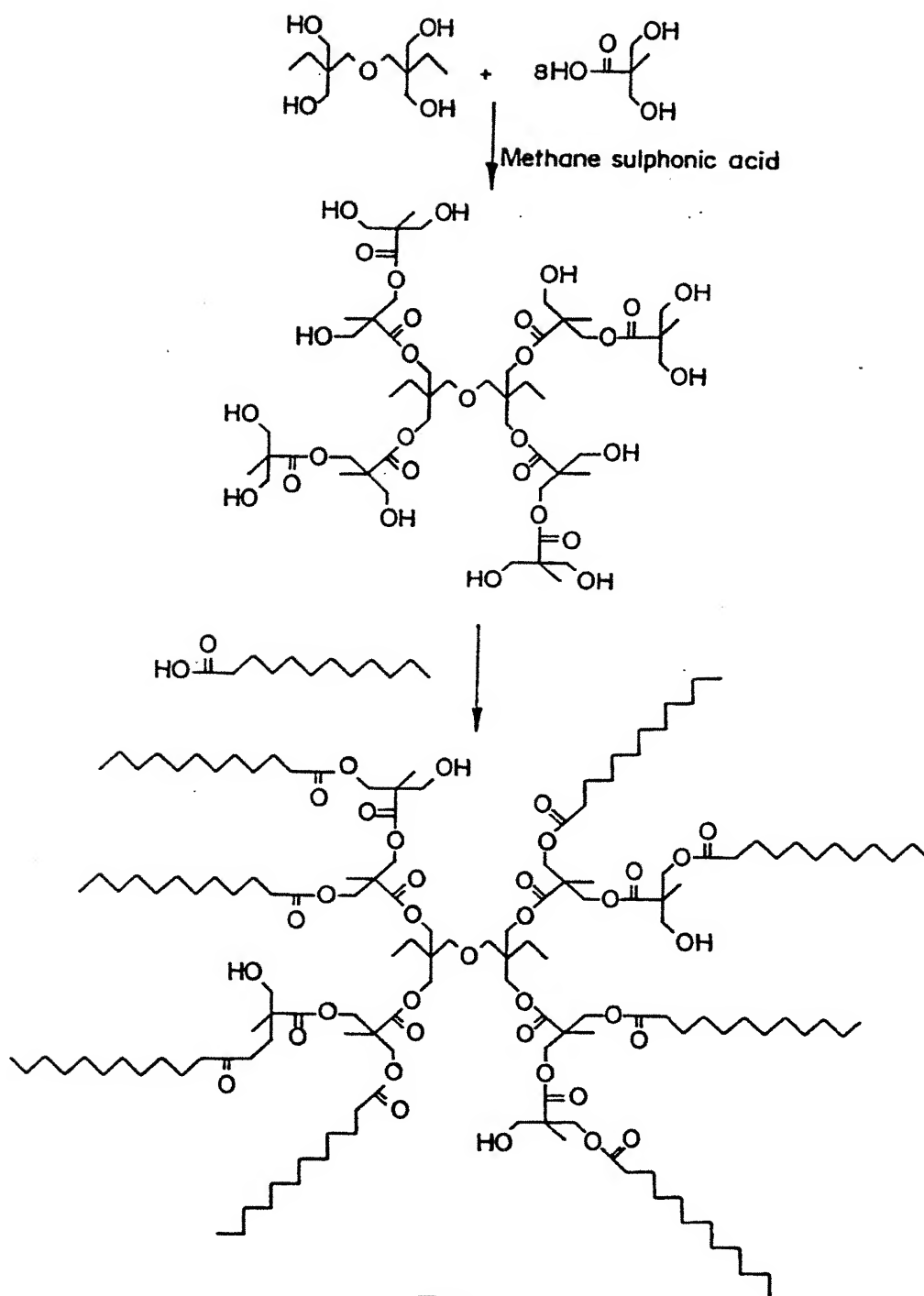


FIG. 1

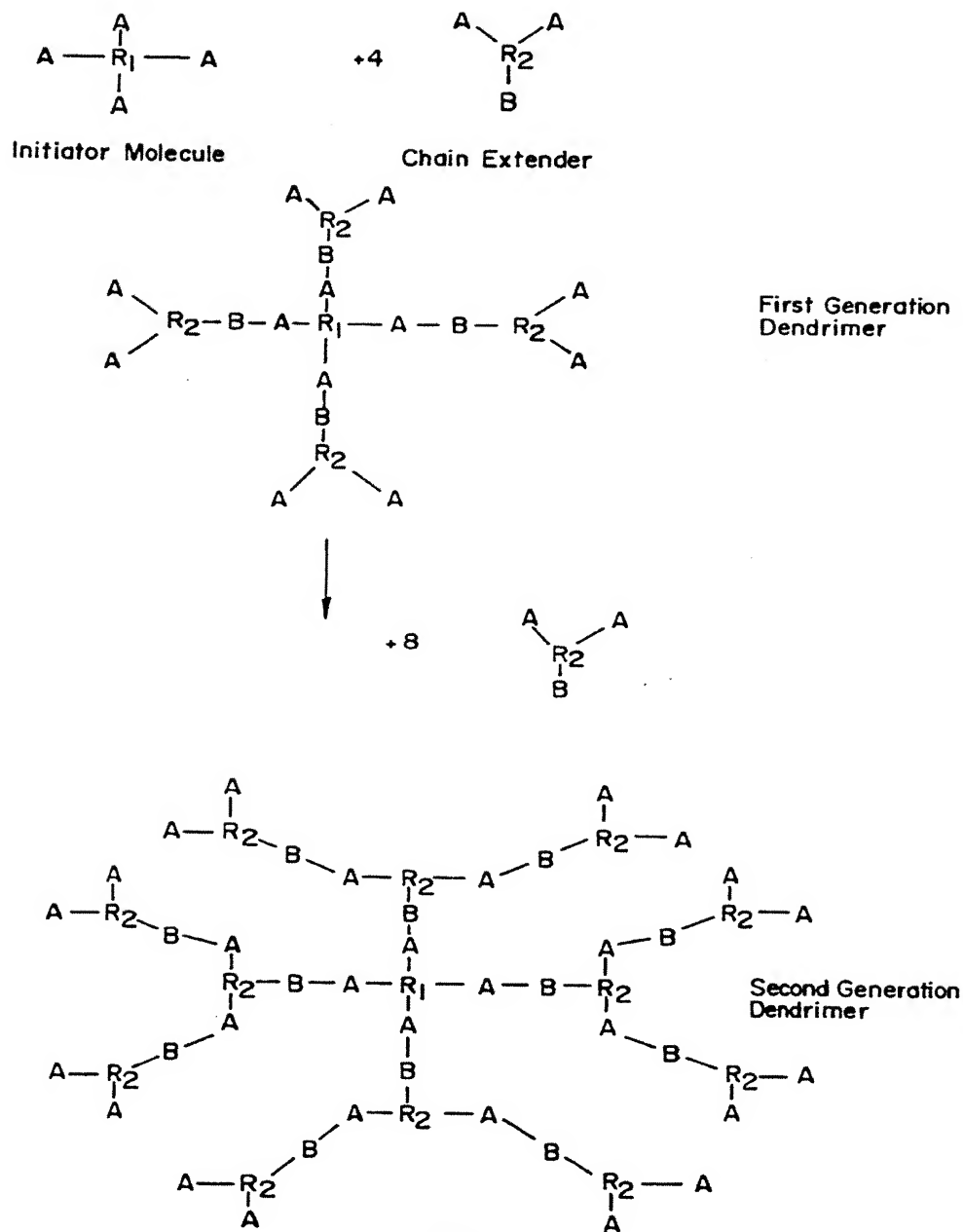


FIG.2

DENDRITIC MACROMOLECULE AND PROCESS FOR PREPARATION THEREOF

This application is a 371 of PCT/SE93/00148 filed Feb. 24, 1993.

The present invention relates to a dendritic macromolecule, comprising composed of a central initiator molecule or initiator polymer having one or more reactive groups (A), which groups (A) under formation of an initial tree structure are bonded to reactive carboxyl groups (B) of a monomeric chain extender containing the two reactive groups (A) and (B). The tree structure is optionally extended and further branched from the initiator molecule or initiator polymer by an addition of further molecules of a monomeric chain extender by means of bonding between the reactive groups (A) and (B) thereof and is optionally further extended by reaction with a chain stopper.

The invention also comprises a process for preparation of the dendritic macromolecule.

Various dendritic macromolecules, so called dendrimers are by Tamalia et al described in Angew. Chem. Int. Ed. Engl. 29 pages 138-175 (1990). The macromolecules hold a tree structure.

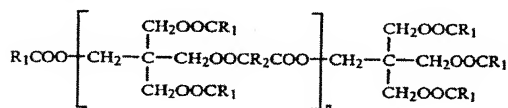
Products quite different from the present invention are in said publication described, which publication discloses the preparation of polyamide amines of the dendrimer type. As initiator molecule are NH_3 used and as chain extender methyl acrylate and ethylene diamine. The yielded macromolecules are NH_2 terminated. Chain stoppers are, according to this process, not used.

However, the present invention refers to a dendritic, that is a hyperbranched, macromolecule of the polyester type.

Ordinary polyesters are well-known and have been manufactured for a very long time. They exhibit many good properties but are also submitted to some drawbacks, which until now have been regarded as impossible to avoid.

An alkyd is a typical example of a polyester type having a very large commercial significance. Alkyds are normally used as components in paint binders.

The composition of an alkyd can be illustrated by the following structural formula



where

R_1 is the alkyl moiety of an unsaturated fatty acid of such a type that it is reactive to air oxygen thereby providing the polyester with air drying properties

R_2 is the alkyl or aryl moiety of a difunctional carboxylic acid

n is the average degree of polymerisation.

An alkyd is most often a high molecular and randomly branched compound with a broad dispersivity, which not is illustrated by above simplified formula. An alkyd exhibits due to this a very high viscosity and large amounts of solvents must thus be added to obtain so low a viscosity that it can be utilised.

Further examples are so called conventional polyesters. They are in principal composed similar to above structural formula, but with the difference that R_1 is the

alkyl moiety of a saturated monofunctional acid and that some of the alcohol moieties in the chain are unesterified, i.e. the polyesters contain unreacted hydroxyl groups. Curing is performed by a crosslinking between the unreacted hydroxyl groups and e.g. a melamine resin. The demand for viscosity reducing solvents is to obtain applicable lacquers in this case also very high.

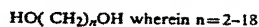
According to the present invention above drawbacks have quite unexpectedly been avoided and a hyperbranched macromolecule of the dendrimer type has been brought about. The dendritic macromolecule according to the invention comprises a central initiator molecule or initiator polymer having one or more reactive groups (A), which groups (A) under formation of an initial tree structure are bonded to reactive groups (B) of a monomeric chain extender holding the two reactive groups (A) and (B), which tree structure optionally is extended and further branched from the initiator molecule or initiator polymer by an addition of further molecules of a monomeric chain extender through bonding between the reactive groups (A) and (B) thereof. The tree structure is optionally further extended by reaction with a chain stopper. The macromolecule is characterised in that the reactive groups (A) and (B) are hydroxyl groups (A) and carboxyl groups (B), respectively, and that the chain extender has at least one carboxyl group (B) and at least two hydroxyl groups (A) or hydroxyalkyl substituted hydroxyl groups (A).

An alkyd having a high molecular weight, as necessary to give good performance characteristics, as well as having so low a viscosity that the alkyd can be used solventless or with only a very small addition of solvents, is obtained when an alkyd is formulated as a dendrimer in accordance with the present invention. An alkyd, which at room temperature is liquid although the molecular weight is very high, can be prepared. Such alkyds are very easy to emulsify in water. A sufficiently hard film is obtained after air drying, provided unsaturated fatty acids or other autoxidatively drying compounds are used as chain stoppers. Naturally, the invention gives due to above great advantages from an environmental point of view.

The central initiator molecule or initiator polymer can suitably consist of

- a) an aliphatic, a cycloaliphatic or an aromatic diol
- b) a triol
- c) a tetrol
- d) a sugar alcohol such as sorbitol and mannitol
- e) anhydroennea-heptitol or dipentaerythritol
- f) an α -alkylglucoside such as α -methylglucoside
- g) a monofunctional alcohol
- h) an alkoxylate polymer having a molecular weight of at most 8000 and which is produced by a reaction between an alkylene oxide or a derivative thereof and one or more hydroxyl groups from any of the alcohols selected from any of the sections a) through g).

The in section a) disclosed diols can be of several different types. They can, thus, be linear having the formula



Diols of above type are for instance 1,3-propanediol, 1,2-ethanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol and polytetrahydrofuran.

The diols can also be branched as for instance dimethylolpropane, neopentyl glycol, 2-propyl-2-methyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,2-propanediol, 1,3-butanediol, 2,2,4-trimethylpentane-1,3-diol, trimethylhexane-1,6-diol, 2-methyl-1,3-propanediol, diethylene glycol, triethylene glycol, polyethylene glycols, dipropylene glycol, tripropylene glycol and polypropylene glycols.

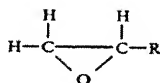
Cycloaliphatic diols such as cyclohexane dimethanol and cyclic formals of pentaerythritol as for instance 1,3-dioxane-5,5-dimethanol can, furthermore, be used.

Aromatic diols, for instance 1,4-xylylene glycol and 1-phenyl-1,2-ethanediol, as well as reaction products of polyfunctional phenolic compounds and alkylene oxides or derivatives thereof, can furthermore be employed. Bisphenol A, hydroquinone and resorcinol are examples of suitable phenolic compounds.

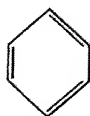
Diols of the ester type, for example neopentylhydroxypivalate, are also suitable diols.

As substitute for a 1,2-diol can corresponding 1,2-epoxide or an α -olefine oxide be used.

A general formula for 1,2-epoxides can be given as



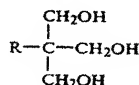
wherein R is H, $\text{CH}_3 \dots \text{C}_n\text{H}_{2n+1}$ or



and $n \geq 2$

Ethylene oxide, propylene oxide, 1,2-butylene oxide and styrene oxide can serve as examples of such compounds.

The under section b) mentioned triols can as the diols be of various types. The general formula can be



wherein R is $\text{C}_n\text{H}_{2n+1}$ and $n \leq 24$.

R can be a linear or branched alkyl moiety. Trimethylolpropane, trimethyloethane, trimethylolbutane, 3,5,5-trimethyl-2,2-dihydroxymethylhexane-1-ol are examples of this type of triols.

A further kind of suitable triols are those having two types of hydroxyl groups, primary as well as secondary hydroxyl groups, as for instance glycerol and 1,2,6-hexanetriol. It is also possible to use cycloaliphatic and aromatic triols and/or corresponding adducts with alkylene oxides or derivatives thereof.

Tetrols as mentioned under section c) above can comprise for example pentaerythritol, ditrimethylolpropane, diglycerol and ditrimethyloethane. It is also possible to use cycloaliphatic and aromatic tetrols as well as corresponding adducts with alkylene oxides or derivatives thereof.

Chain extenders used according to the invention can suitably consist of

a) a monofunctional carboxylic acid having at least two hydroxyl groups.

b) a monofunctional carboxylic acid having at least two hydroxyl groups wherein one or more of the hydroxyl groups are hydroxyalkyl substituted.

The chain extender can advantageously comprise α, α -bis(hydroxymethyl) propionic acid (dimethylolpropionic acid), α, α -bis-(hydroxymethyl)-butyric acid, α, α -tris(hydroxymethyl)-acetic acid, α, α -bis(hydroxymethyl)-valeric acid, α, α -bis(hydroxy)propionic acid or α -phenylcarboxylic acids having at least two hydroxyl groups directly pendant to the phenyl ring (phenolic hydroxyl groups) such as 3,5-dihydroxybenzoic acid.

Above acids wherein one or more of the hydroxyl groups are hydroxyalkyl substituted, can possibly also be used as chain extenders.

The dendritic macromolecule can in certain cases also contain a chain stopper, which advantageously is selected among compounds from one or more of the following sections

a) a saturated monofunctional carboxylic acid or a saturated fatty acid or an anhydride thereof

b) an unsaturated fatty acid

c) an unsaturated monofunctional carboxylic acid

d) a diisocyanate or an oligomer thereof

e) an adduct of a reaction product formed by means of a compound according to section d)

f) a difunctional or a polyfunctional carboxylic acid or an anhydride thereof

g) an adduct of a reaction product formed by means of a compound according to section f)

h) an aromatic monofunctional carboxylic acid such as benzoic acid and para-tert.butylbenzoic acid

i) an epihalohydrin such as 1-chloro-2,3-epoxy propane and 1,4-dichloro-2,3-epoxy butane

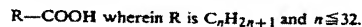
j) a glycidyl ester of a monofunctional carboxylic acid or of a fatty acid, which acids hold 1-24 carbon atoms

k) an epoxide of an unsaturated fatty acid with 3-24 carbon atoms such as epoxidized soybean fatty acid

The terminal hydroxyl groups in the chain of the macromolecule can of course to a larger or smaller extent be reacted with a chain stopper. Important aspects on the use and choice of chain stoppers are for instance created by the desired properties of the prepared macromolecule.

The choice of chain stopper is particularly important with regard to adjusting the properties of the macromolecule. A certain chain stopper is normally used for a certain application area, while other application areas employ other chain stoppers.

A chain stopper according to section a) above, comprising a saturated monofunctional carboxylic acid or a fatty acid, is described by the following general formula



Above carboxylic or fatty acid can be linear or branched and can be employed as acid or, where applicable, as anhydride. Examples are acetic acid, propionic acid, butyric acid, valeric acid, isobutyric acid, trimethylacetic acid, caproic acid, caprylic acid, heptanoic acid, capric acid, pelargonic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, lignoceric

acid, ceratic acid, montanoic acid, isostearic acid, isononanoic acid and 2-ethylhexanoic acid.

According to section b) above, the chain stopper can be an unsaturated fatty acid as for instance oleic acid, ricinoleic acid, linoleic acid, linolenic acid, erucic acid, soybean fatty acid, linseed fatty acid, dehydrated castor fatty acid, tall oil fatty acid, tung oil fatty acid, sunflower fatty acid and safflower fatty acid.

An unsaturated monofunctional carboxylic acid, in accordance with section c) above, can also be used as chain stopper. Examples of such acids are acrylic acid and methacrylic acid.

Section d) above has bearing on the use of diisocyanates and oligomers thereof as chain stoppers. Compounds belonging to this section can be exemplified by toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, diphenylmethane diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, 4,4-diisocyanato-dicyclohexylmethane, 1,5-diisocyanatonaphthalene, 1,4-phenylene diisocyanate, tetramethyl xylene diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 1,4-diisocyanate cyclohexane, 1,3-diisocyanate benzene and 1,4-diisocyanate benzene.

Adducts prepared from reaction products formed by means of a component from section d) above can, furthermore, be used as chain stoppers in accordance with section e). Chain stoppers of this kind are for instance adducts with hydroxyethyl acrylate and hydroxypropyl acrylate, trimethylolpropane diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate and corresponding acrylates of alkoxyolated trimethylolpropane and pentaerythritol, respectively. Further examples are adducts with hydroxysubstituted allyl ethers such as trimethylolpropane diallyl ether and pentaerythritol triallyl ether.

Polyfunctional carboxylic acids and/or corresponding anhydrides are as disclosed in section f) above also suitable as chain stoppers and can be exemplified by maleic anhydride, fumaric acid, orthophthalic anhydride, terephthalic acid, isophthalic acid, adipic acid, azelaic acid, sebacic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, succinic acid and trimellitic anhydride.

Adducts prepared from reaction products formed by means of a component from section f) can, according to section g) above, be used as chain stoppers. Examples are i.a. adducts of hydroxysubstituted allyl ethers such as adducts of trimethylolpropane monoallyl ether, trimethylolpropane diallyl ether, pentaerythritol triallyl ether and glycerol monoallyl ether.

Epihalohydrins as disclosed in section i) above can suitably be used as chain stoppers, thus yielding epoxy functional dendritic macromolecules.

A glycidyl ester of a monofunctional carboxylic acid or of a fatty acid, which acids hold 1-24 carbon atoms, can according to section j) above, be used as chain stoppers. Such compounds can be exemplified by 1,2-epoxy-3-allyloxypropane, 1-allyloxy-2,3-epoxypropane, 1,2-epoxy-3-phenoxypropane and 1-glycidyoxy-2-ethylhexane.

Epoxy functional dendrimers can, also, be prepared through epoxidation of an unsaturation which is incorporated in the terminated dendrimer, for example a fatty acid unsaturation.

It is also possible to use adducts of such epoxy compounds as glycidyl ether of bisphenol A and oligomers thereof.

The present invention also comprises a process for preparation of a dendritic macromolecule as disclosed above. The process is characterised in that an initiator molecule or an initiator polymer having one or more hydroxyl groups are reacted at a temperature of 0°-300° C. such as 50°-280° C., preferably 100°-250° C., with a chain extender having one carboxyl group and at least two hydroxyl groups or hydroxyalkyl substituted hydroxyl groups. The reaction product obtained is thereafter potentially reacted with a chain stopper.

The molar ratio between the number of moles used chain extender per mole hydroxyl groups originating from the initiator molecule or initiator polymer is suitably to be found between 1:1 and 2000:1, preferably between 1:1 and 1100:1. In certain cases the ratio is between 1:1 and 500:1 such as between 1:1 and 100:1.

It is advisable to continuously remove water formed during the reaction. Suitable methods are for instance inlet of an inert gas into the reaction vessel, vacuum distillation, azeotropic distillation or the like.

The reaction can be carried out without using any catalyst. An ordinary esterification catalyst is, however, used in many cases and is then suitably selected among

a) a Bronstedt acid such as naphthalene sulphonic acid, para-toluene sulphonic acid, methane sulphonic acid, trifluoromethane sulphonic acid, trifluoroacetic acid, sulphuric acid or phosphoric acid

b) a Lewis acid such as BF_3 , AlCl_3 , SnCl_4

c) a titanate as tetrabutyl titanate

d) zinc powder or an organozinc compound

e) tin powder or an organotin compound

The initial step is preferably performed in the presence of an acid catalyst and the product thus obtained can, if necessary, be neutralised prior to a reaction with a chain stopper.

Initiator molecules or polymers as well as chain extenders used in the process according to the invention are disclosed above.

Potential chain stoppers used in the process according to the invention are also disclosed above.

The initiator molecule consists, at a preferred embodiment of the process according to the invention, of ditrimethylolpropane, ditrimethylolethane, dipentaerythritol, pentaerythritol, alkoxyolated pentaerythritol, trimethylolethane, trimethylolpropane, alkoxyolated trimethylolpropane, glycerol, neopentyl glycol, dimethylolpropane or 1,3-dioxane-5,5-dimethanol. The chain extender consists, at this preferred embodiment of dimethylolpropionic acid, α,α -bis(hydroxymethyl)-butyric acid, α,α,α -tris(hydroxymethyl)-acetic acid, α,α -bis(hydroxymethyl)-valeric acid, α,α -bis(hydroxy)-propionic acid or 3,5-dihydroxybenzoic acid.

The initiator molecule consists, at an especially preferred embodiment of the process according to the invention, of ditrimethylolpropane, trimethylolpropane, ethoxylated pentaerythritol, pentaerythritol or glycerol while the chain extender consists of dimethylolpropionic acid.

The invention also refers to the use of a dendritic macromolecule according to above as component in applications such as alkyds, alkyd emulsions, saturated polyesters, unsaturated polyesters, epoxy resins, phenolic resins, polyurethane resins, polyurethane foams and elastomers, binders for radiation curing systems such as systems cured with ultra-violet (UV) and infra-red (IR) light or electron-beam (EB), dental materials, adhesives,

synthetic lubricants, microlithographic paints, binders for powder systems, amino resins, composites reinforced with glass, aramid or carbon/graphite fibres and moulding compounds based on urea-formaldehyde resins, melamineformaldehyde resins or phenol-formaldehyde resins.

The invention is further explained in connection to below embodiment Examples, of which Examples 1-12 and 15-52 refer to preparations and evaluations of various dendritic products within the scope of the invention, while Examples 13 and 14 are comparative experiments related to conventional products beyond the scope of the invention.

The embodiment Examples disclose as follows
Examples 1-7, 27-30 and 48: Preparations of polyesters based on various initiator molecules and dimethylolpropionic acid.

Examples 8-12, 31-34, 42 and 49: Preparations of alkyds based on polyesters, prepared according to preceding Examples, and unsaturated fatty acids.

Examples 13 and 14: Preparations of conventional alkyds. These Examples are comparative experiments beyond the scope of the present invention.

Examples 15, 17, 22-23, 25-26, 43 and 47: Lacquer formulations and evaluations of products according to preceding Examples.

Examples 16, 18, 37 and 38: Functionalization of polyesters, prepared according to preceding Examples, with mixtures of capric and caprylic acid.

Example 19: Preparation of an intermediate product intended to be used in Examples 20 and 21.

Examples 20 and 21: Preparations of unsaturated polyesters based on i.a. the intermediate product prepared according to Example 19.

Examples 24, 39 and 40: Preparations of acrylates based on products prepared according to preceding Examples.

Examples 35 and 36: Preparations of alkyd emulsions based on alkyds prepared according to Examples 29 and 30.

Examples 41 and 50: Preparations of epoxy resins based on products according to Examples 37 and 49.

Example 51: Preparation and structural characterisation of a 9 generations dendritic polyester. Characterisation by the Mark-Houwink constant.

Example 52: Preparation of a polyurethane dispersion. Evaluation results with reference to Examples above are given in Tables 1-7, of which

Table 1 gives results from Examples 1-7.

Table 2 gives results from Examples 8-14.

Table 3 gives results from Examples 20-21.

Table 4 gives results from Examples 22-23.

Table 5 gives results from Example 24.

Table 6 gives results from Examples 39-40.

Table 7 gives results from Examples 31-36.

The invention is also illustrated by the enclosed FIGS. 1 and 2, of which

FIG. 1 gives a general outline of a reaction between an initiator molecule of ditrimethylolpropane and a chain extender of dimethylolpropionic acid forming a 1.5 generation dendrimer. A chain stopper consisting of lauric acid is thereafter added in a final reaction step. The initial step is performed using methane sulphonic acid as catalyst.

FIG. 2 gives a general outline of a 2 generations dendrimer prepared by a reaction between an initiator molecule holding four hydroxyl groups A and a chain extender with two hydroxyl groups A and one carboxyl

group B. The reaction can, of course, be further continued and hence the molecule chains be still more branched.

EXAMPLE 1

1.0 mole of ditrimethylolpropane was charged in a 4-necked reaction flask equipped with a stirrer, argon inlet, a thermometer and a cooler for water separation. The temperature was raised to 120° C. and 8.0 moles of dimethylolpropionic acid together with 0.12 mole of para-toluene sulphonic acid were added. The temperature was thereafter raised to 140° C. and a stream of argon was allowed to pass through the reaction flask in order to remove formed reaction water. After 2 hours, 8.0 moles of lauric acid were charged and the reaction was allowed to continue for a further 2 hours.

The viscosity of obtained polyester was 10 Pas at 23° C. Further properties are given in Table 1.

EXAMPLE 2

The procedure according to Example 1 was repeated with the difference that 4.0 moles of lauric acid instead of 8.0 moles were charged.

The viscosity of obtained polyester was 1037 Pas at 23° C. Further properties are given in Table 1.

EXAMPLE 3

The procedure according to Example 1 was repeated with the difference that 12.0 moles of lauric acid instead of 8.0 moles were charged.

The viscosity of obtained polyester was 1.5 Pas at 23° C. Further properties are given in Table 1.

EXAMPLE 4

The procedure according to Example 1 was repeated with the difference that 4.0 moles of dimethylolpropionic acid instead of 8.0 moles and that 5.33 moles of lauric acid instead of 8.0 moles were charged.

The viscosity of obtained polyester was 3.9 Pas at 23° C. Further properties are given in Table 1.

EXAMPLE 5

The procedure according to Example 1 was repeated with the difference that 4.0 moles of dimethylolpropionic acid instead of 8.0 moles were charged.

The viscosity of obtained polyester was 0.73 Pas at 23° C. Further properties are given in Table 1.

EXAMPLE 6

The procedure according to Example 1 was repeated with the difference that 12.0 moles of dimethylolpropionic acid instead of 8.0 moles and that 10.67 moles lauric acid instead of 8.0 moles were charged.

The viscosity of obtained polyester was 18.4 Pas at 23° C. Further properties are given in Table 1.

EXAMPLE 7

The procedure according to Example 1 was repeated with the difference that 12.0 moles of dimethylolpropionic acid instead of 8.0 moles and that 16.0 moles lauric acid instead of 8.0 moles were charged.

The viscosity of obtained polyester was 2.6 Pas at 23° C. Further properties are given in Table 1.

EXAMPLE 8

1.0 mole of ditrimethylolpropane was charged in a 4-necked reaction flask equipped with a stirrer, nitrogen inlet, a thermometer and a cooler for water separation.

9

The temperature was raised to 120° C. and 8.0 moles of dimethylolpropionic acid together with 10.7 g of methane sulphonic acid were added. The temperature was thereafter raised to 140° C. and maintained until the water distillation had ceased. A vacuum of 15 mm Hg was thereafter applied for 30 minutes followed by an addition of 8.6 g of Ca(OH)₂ for neutralisation of the methane sulphonic acid. After 15 minutes, 10.0 moles of soybean fatty acid and 3% by weight of xylene were charged (the amount of xylene was calculated on the subtotal of all included components). The temperature was raised to 230° C. and maintained until an acid value of 4.5 mg KOH/g was obtained. A vacuum of 15 mm Hg was thereafter applied to evaporate the xylene.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	1160 mpas
Gardner colour value	5
Hydroxyl value	21 mg KOH/g
Molecular weight M_n	3910 g/mole
Molecular weight M_w	6790 g/mole
$M_w/M_n = H$	1.7

EXAMPLE 9

The procedure according to Example 8 was repeated with the difference that 8.0 moles of soybean fatty acid and that 2.0 moles of benzoic acid were charged instead of 10.0 moles of soybean fatty acid.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	2950 mpas
Gardner colour value	6
Hydroxyl value	32 mg KOH/g
Acid value	2.8 mg KOH/g

EXAMPLE 10

1.0 mole of ditrimethylolpropane was charged in a 4-necked reaction flask equipped with a stirrer, nitrogen inlet, a thermometer and a cooler for water separation. The temperature was raised to 120° C. and 4.0 moles of dimethylolpropionic acid together with 5.4 g of methane sulphonic acid were added. The temperature was thereafter raised to 140° C. and maintained until the water distillation had ceased. A vacuum of 15 mm Hg was thereafter applied for 30 minutes followed by an addition of 4.3 g of Ca(OH)₂ for neutralisation of the methane sulphonic acid. After 15 minutes, 7.0 moles of soybean fatty acid and 3% by weight of xylene were charged (the amount of xylene was calculated on the subtotal of all included components). The temperature was raised to 230° C. and maintained until an acid value of 4.7 mg KOH/g was obtained. A vacuum of 15 mm Hg was thereafter applied to evaporate the xylene.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	620 mPas
Gardner colour value	5

EXAMPLE 11

1.0 mole of ditrimethylolpropane was charged in a 4-necked reaction flask equipped with a stirrer, nitrogen inlet, a thermometer and a cooler for water separation.

10

The temperature was raised to 120° C. and 12.0 moles of dimethylolpropionic acid together with 16.0 g of methane sulphonic acid were added. The temperature was thereafter raised to 140° C. and maintained until the water distillation had ceased. A vacuum of 15 mm Hg was thereafter applied for 30 minutes followed by an addition of 12.9 g of Ca(OH)₂ for neutralisation of the methane sulphonic acid. After 15 minutes, 13.0 moles of soybean fatty acid and 3% by weight of xylene were charged (the amount of xylene was calculated on the subtotal of all included components). The temperature was raised to 230° C. and maintained until an acid value of 5.4 mg KOH/g was obtained. A vacuum of 15 mm Hg was thereafter applied to evaporate the xylene.

Obtained product exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	2060 mPas
Gardner colour value	5

EXAMPLE 12

1.0 mole of trimethylolpropane was charged in a 4-necked reaction flask equipped with a stirrer, nitrogen inlet, a thermometer and a cooler for water separation. The temperature was raised to 120° C. and 9.0 moles of dimethylolpropionic acid together with 12.0 g of methane sulphonic acid were added. The temperature was thereafter raised to 140° C. and maintained until the water distillation had ceased. A vacuum of 15 mm Hg was thereafter applied for 30 minutes followed by an addition of 9.7 g of Ca(OH)₂ for neutralisation of the methane sulphonic acid. After 15 minutes, 10.0 moles of soybean fatty acid and 3% by weight of xylene were charged (the amount of xylene was calculated on the subtotal of all included components). The temperature was raised to 230° C. and maintained until an acid value of 7.3 mg KOH/g was obtained. A vacuum of 15 mm Hg was thereafter applied to evaporate the xylene.

Obtained product exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	1180 mPas
Gardner colour value	6

EXAMPLE 13

(Comparative Experiment)

841.7 g of isophthalic acid, 116.3 g of pentaerythritol, 551.1 g of soybean fatty acid and 3% by weight of xylene were charged in a 4-necked reaction flask equipped with a stirrer, a thermometer, nitrogen inlet and a cooler provided with a water trap (Dean-Stark) for separation of formed reaction water (the amount of xylene was calculated on subtotal of all included components). The temperature was during 90 minutes raised to 230° C. and maintained until an acid value of 5.0 mg KOH/g was obtained. A vacuum of 15 mm Hg was thereafter applied to evaporate the xylene.

Obtained conventional alkyd exhibited the following properties:

Nonvolatile content	100%
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-continued

Viscosity at 23° C.	1900 mPas
Gardner colour value	4
Hydroxyl value	42 mg KOH/g

As will be seen on a comparison between the results from Examples 8 and 13, as given in Table 2, the alkyd according to the invention (Ex. 8) exhibits a faster hardness growth and a shorter drying time.

EXAMPLE 14

(Comparative Experiment)

841.7 g of soybean oil, 207.6 g of pentaerythritol and 0.015% litharge were charged in a 4-necked reaction flask equipped with a stirrer, a thermometer, nitrogen inlet and a cooler provided with a water-trap (Dean-Stark) for separation of reaction water. The temperature was raised to 240° C. and maintained until 1 part of the reaction mixture was completely soluble in 3 parts of methanol. The temperature was then reduced to 170° C. and 351.3 g of o-phthalic anhydride together with 3% by weight of xylene were charged (the amount of xylene was calculated on subtotal of all included components). Thereafter the temperature was raised to 240° C. and maintained until an acid value of 6.1 mg KOH/g was obtained.

Obtained conventional alkyd exhibited diluted in white spirit the following properties:

Nonvolatile content	62.5%
Viscosity at 23° C.	2880 mPas
Gardner colour value	6

As will be seen on a comparison between the results from Examples 11 and 14, as given in Table 2, the alkyd according to the invention (Ex. 11) exhibits a faster hardness growth and a shorter drying time.

EXAMPLE 15

The following driers were mixed with the products according to Examples 8-14:

Zirconium salt	0.25%
Cobalt salt	0.06%
Calcium salt	0.05%

Above percentages were calculated as 100% metal on the non-volatile content of the products.

An antiskin agent (Exkin 2, Servo B.V., The Netherlands) was, furthermore, added in an amount of 0.30%.

The thus prepared lacquers were coated on glass panels.

The hardness was recorded with a König Pendulum after 5, 8 and 24 hours of drying at 23°±2° C. and 50±5% relative humidity. The filmthickness was 45±5 µm (dry).

The drying time was measured using a so called Beck-Koller Recorder. The filmthickness was 35±5 µm (dry).

The results are given in Table 2.

EXAMPLE 16

1.0 mole of ditrimethylolpropane was charged in a 4-necked reaction flask equipped with a stirrer, nitrogen inlet, a thermometer and a cooler for water separation. The temperature was raised to 120° C. and 12.0 moles of

dimethylolpropionic acid together with 16.0 g of methane sulphonic acid were added. The temperature was thereafter raised to 140° C. and maintained until the water distillation had ceased. A vacuum of 15 mm Hg was thereafter applied for 30 minutes followed by an addition of 12.9 g of Ca(OH)₂ for neutralisation of the methane sulphonic acid. After 15 minutes, 9.0 moles of a mixture of caprylic and capric acid together with 3% by weight of xylene were charged (the amount of xylene was calculated on the subtotal of all included components). The temperature was raised to 210° C. and maintained until an acid value of 3.2 mg KOH/g was obtained. A vacuum of 15 mm Hg was thereafter applied to evaporate the xylene.

Obtained product exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	68800 mPas
Gardner colour value	3-4
Hydroxyl value	127 mg KOH/g

EXAMPLE 17

The alkyd prepared according to Example 16 was mixed with a hexamethoxymethyl melamine resin at a weight ratio of 70:30 (alkyd:melamine resin), calculated as dry products. The mixture was diluted with xylene/isobutanol (80:20 by weight) to a nonvolatile content of 80% and p-Toluene sulphonic acid was added as curing catalyst.

The thus produced lacquer had a viscosity of 580 mPas at 23° C.

The lacquer was coated on glass panels at a filmthickness of 35±5 µm (dry) and cured at 160° C. for 10, 20 and 30 minutes. The film hardness was by means of a König Pendulum determined after conditioning at 23°±2° C. and 50±5 relative humidity.

The following results were obtained:

Curing Time at 160° C.	Pendulum Hardness König seconds
10	67
20	70
30	70

EXAMPLE 18

A synthetic lubricant was prepared using the same procedure as according to Example 16, with the difference that 13.0 moles of a mixture of caprylic and capric acid were charge instead of 9.0 moles.

Obtained product exhibited the following properties:

Nonvolatile content	99.8%
Viscosity at 23° C.	9400 mPas
Acid value	2.6 mg KOH/g
Hydroxyl value	44 mg KOH/g

EXAMPLE 19

1.0 mole of trimethylolpropane diallyl ether, 2.5 moles of maleic anhydride and a catalytic amount of para-toluene sulphonic acid were charged in a 3-necked reaction flask and dissolved in 1.5 liter of toluene. The

temperature was, under stirring and argon purge, raised to 70° C. and the reaction was allowed to continue for 16 hours. The reaction mixture was thereafter repeatedly washed with distilled water, in order to remove the excess of maleic anhydride, and thereafter dried with MgSO₄. Prepared intermediate product was used in below examples 20 and 21.

EXAMPLE 20

1.0 mole of ditrimethylolpropane was charged in a 4-necked reaction flask equipped with a stirrer, argon inlet, a thermometer and a cooler for water separation. The temperature was raised to 120° C. and 8.0 moles of dimethylolpropionic acid together with 16.0 g of methane sulphonic acid were added. The temperature was thereafter raised to 140° C. and a stream of argon was allowed to pass through the reaction flask in order to remove formed reaction water. After 2 hours, were 3.0 moles of lauric acid charged. The reaction was thereafter allowed to continue for another 2 hours, after which the temperature was reduced to 120° C. and a vacuum of 12 mm Hg was applied during 30 minutes. A catalytic amount of hydroquinone and 6.0 moles of trimethylolpropane diallyl ether maleate, according to Example 19, were charged. The reaction was allowed to continue for 8 hours before the resin was cooled.

Obtained properties are given in Table 3.

EXAMPLE 21

The procedure according to Example 20 was repeated with the difference that no lauric acid was charged and that 9.0 moles of trimethylolpropane diallyl ether maleate, according to Example 19, were added instead of 6.0 moles.

Obtained properties are given in Table 3.

EXAMPLE 22

1.5 g of the resin according to Example 20 were mixed with the following amounts of initiators

0.06540 g of cobalt octoate (6% in butyl acetate)
0.00230 g of N,N-dimethyl aniline (10% in butyl acetate)

0.01980 g of benzoyl peroxide (10% in butyl acetate)
0.03460 g of tert.butyl perbenzoate (50% in butyl acetate)

0.00028 g of hydroquinone (2.5% in butyl acetate)

Resulting lacquer was coated on glass panels at a filmthickness of 25±5 μm (dry). The layers were after a flash off time of 10 minutes at room temperature cured at 80° C. for 20, 30, 40, 50 and 60 minutes. The film hardness was measured by means of a König Pendulum.

Obtained properties are given in Table 4.

EXAMPLE 23

Example 22 was repeated with the difference that 1.5 g of the resin according to Example 21 was used.

Obtained properties are given in Table 4.

EXAMPLE 24

0.25 mole of ditrimethylolpropane was charged in a 4-necked reaction flask equipped with a stirrer, gas/air inlet, a thermometer and a cooler provided with a water-trap (Dean-Stark). The temperature was raised to 120° C. and 3.0 moles of dimethylolpropionic acid together with 4.0 g of methane sulphonic acid were added. The temperature was thereafter raised to 140° C. and a stream of argon was allowed to pass through the reaction flask in order to remove formed reaction wa-

ter. The temperature was after 2 hours of reaction reduced to 115° C. and argon was replaced by air. 5.0 moles of acrylic acid, 770.0 g of toluene, 1.1 g of methyl hydroquinone and 0.11 g of nitrobenzene were now charged and the temperature was raised to reflux. Formed reaction water was thus removed by azeotropic distillation. The reaction mixture was after 20 hours, when the theoretical amount of reaction water had been collected, cooled to room temperature.

The room tempered reaction mixture was, in order to obtain a purification of obtained acrylate oligomer, allowed to pass through a column packed with silica gel and aluminium oxide using toluene as eluent.

Toluene was finally evaporated under vacuum with a minor air stream passing through the product.

EXAMPLE 25

The acrylate oligomer according to Example 24 was UV-cured as sole binder as well as in a 50:50 (by weight) mixture with tripropylene glycol diacrylate. A photoinitiator (Irgacure 184, Ciba-Geigy, Switzerland) was added in an amount of 3%.

Resulting lacquers were coated on glass panels at a filmthickness of 30±5 μm (dry) and were UV-cured using a belt speed of 12.4 m/min. and two UV-lamps. The film hardness was measured by means of a König Pendulum.

Obtained properties are given in Table 5.

EXAMPLE 26

The polyester according to Example 2 was mixed with a cycloaliphatic diepoxy resin (Cyracure UVR 6100, Union Carbide, USA) at a weight ratio of 35:65. Three parts of a thermal iodonium salt were added as curing catalyst.

Resulting lacquer was coated on glass panels at a filmthickness of 25±5 μm and was allowed to cure for 10 minutes at 120° C. The film hardness was by means of a König Pendulum determined to be 216 König seconds.

EXAMPLE 27

0.85 mole (308.9 g) of Polyol PP 50 (ethoxylated pentaerythritol, Perstorp Polyols, Sweden) and 0.005 mole (0.46 g) of sulphuric acid were charged in a 4-necked reaction flask equipped with a stirrer, a pressure gauge, a cooler and a receiver. The temperature was raised to 140° C. and 3.42 moles (460.5 g) of dimethylolpropionic acid were during 10 minutes added. When charged dimethylolpropionic acid was completely dissolved thus giving a clear solution, the pressure was reduced to 30–40 mm Hg and the reaction was, under stirring, allowed to continued for 4 hours until an acid value of 7.0 mg KOH/g was reached. 6.84 moles (921.0 g) of dimethylolpropionic acid and 0.010 mole (0.92 g) of sulphuric acid were now during 15 minutes added to the reaction mixture. A vacuum of 30–40 mm Hg was, when a clear solution was obtained, applied. The reaction was thereafter, under stirring, allowed to continue for a further 3 hours, after which time the acid value was determined to be 10.2 mg KOH/g.

The hydroxyl value of prepared polyester was 498 mg KOH/g, corresponding to a theoretical hydroxyl value of 501 mg KOH/g.

EXAMPLE 28

0.40 mole (144.6 g) of Polyol PP 50 (ethoxylated pentaerythritol, Perstorp Polyols, Sweden), 3.21 moles

15

(432.0 g) of dimethylolpropionic acid and 0.005 mole (0.45 g) of sulphuric acid were charged in a 4-necked reaction flask equipped as in Example 27. The temperature was raised to 140° C. A vacuum of 30–40 mm Hg was, when a clear solution was obtained, applied. The reaction was, under stirring, allowed to continue for 3 hours, after which time the acid value was determined to be 7.1 mg KOH/g. 8.01 moles (1080.0 g) of dimethylolpropionic acid and 0.01 mole (1.08 g) of sulphuric acid were now during 15 minutes added to the reaction mixture. A vacuum of 30–40 mm Hg was applied as soon as charged dimethylolpropionic acid was dissolved, thus giving a clear solution. The reaction was, under stirring, now allowed to continue for a further 4 hours giving a final acid value of 10.9 mg KOH/g.

The hydroxyl value of prepared polyester was 489 mg KOH/g, corresponding to a theoretical hydroxyl value of 486 mg KOH/g.

EXAMPLE 29

0.05 mole (18.1 g) of Polyol PP 50 (ethoxylated pentaerythritol, Perstorp Polyols, Sweden), 3.0 moles (405.0 g) of dimethylolpropionic acid and 0.009 mole (0.84 g) of sulphuric acid were charged in a 4-necked reaction flask equipped as in Example 27. The temperature was raised to 140° C. A vacuum of 30–40 mm Hg was, when a clear solution was obtained, applied. The reaction was, under stirring, allowed to continue for 1 hour, after which time the acid value was determined to be 28.0 mg KOH/g. 9.6 moles (1296.0 g) of dimethylolpropionic acid and 0.03 mole (2.7 g) of sulphuric acid were now during 20 minutes added to the reaction mixture. A vacuum of 30–40 mm Hg was applied as soon as charged dimethylolpropionic acid was dissolved, thus giving a clear solution. The reaction was now allowed to continued for a further 2 hours giving a final acid value of 23.5 mg KOH/g.

The hydroxyl value of prepared polyester was 468 mg KOH/g, corresponding to a theoretical hydroxyl value of 462 mg KOH/g.

EXAMPLE 30

200.0 g of the polyester according to Example 27, 245.6 g (1.82 mole) of dimethylolpropionic acid and 0.24 g (0.003 mole) of sulphuric acid were charged in a 4-necked reaction flask equipped as in Example 27. The temperature was raised to 140° C. A vacuum of 30–40 mm Hg was, when a clear solution was obtained, applied. The reaction was allowed to continue for 3 hours, after which time the acid value was determined to be 6.7 mg KOH/g. 491.4 g (3.65 moles) of dimethylolpropionic acid and 0.48 g (0.006 mole) of sulphuric acid were now added to the reaction mixture. A vacuum of 30–40 mm Hg was applied as soon as charged dimethylolpropionic acid was dissolved, thus giving a clear solution. The reaction was, under stirring, allowed to continue for a further 7 hours giving a final acid value of 7.8 mg KOH/g.

EXAMPLE 31

400.0 g of the polyester according Example 27, 938.0 g (3.29 moles) of tall oil fatty acid and 0.30 g (0.004 mole) of $\text{Ca}(\text{OH})_2$ were charge in a 4-necked reaction flask equipped as in Example 27. The temperature was raised to 130° C. followed by an addition of a further 0.30 g of $\text{Ca}(\text{OH})_2$. The temperature was thereafter raised to 230° C. and a vacuum of 30–40 mm Hg was applied. After 3 hours of reaction, an esterification cata-

16

lyst (Fascat 4100, Atochem, The Netherlands) was added in an amount of 1.0 g. The reaction was, under stirring and a vacuum of 30–40 mm Hg, now allowed to continue for a further hour, after which time the acid value was determined to be 8.2 mg KOH/g. Obtained alkyd was, to remove suspended particles, finally filtered under pressure.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100 %
Viscosity at 23° C.	1800 mPas
Gardner colour value	5–6

EXAMPLE 32

220.0 g of the polyester according to Example 28 and 500.4 g (1.76 mole) of tall oil fatty acid were charged in a 4-necked reaction flask equipped as in Example 27. The temperature was raised to 140° C. followed by an addition of $\text{Ca}(\text{OH})_2$ in an amount of 1.0 g. A vacuum of 30–40 mm Hg was thereafter applied and the temperature was raised to 230° C. The reaction was, under stirring, allowed to continue for 7 hours, after which time the acid value was determined to be 9.4 mg KOH/g. Obtained alkyd was, to remove suspended particles, finally filtered under pressure.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	14000 mPas

Dissolved in ethanol above alkyd exhibited the following properties:

Nonvolatile content	85%
Viscosity at 23° C.	1240 mPas
Gardner colour value	5–6

EXAMPLE 33

220.0 g of the polyester according to Example 29 and 492.0 g (1.73 mole) of tall oil fatty acid were charged in a 4-necked reaction flask equipped as in Example 27. The temperature was raised to 140° C. followed by an addition of $\text{Ca}(\text{OH})_2$ in an amount of 1.0 g. A vacuum of 30–40 mm Hg was thereafter applied and the temperature was raised to 230° C. The reaction was, under stirring, allowed to continue for 10 hours, after which time the acid value was determined to be 9.5 mg KOH/g. Obtained alkyd was, to remove suspended particles, finally filtered under pressure.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	43500 mPas

Dissolved in ethanol above alkyd exhibited the following properties:

Nonvolatile content	85%
Viscosity at 23° C.	3000 mPas
Gardner colour value	5–6

17

EXAMPLE 34

300.0 g of the polyester according to Example 30, 675.7 g (2.37 moles) of tall oil fatty acid, 0.5 g of an esterification catalyst (Fascat 4100, Atochem, The Netherlands) and 0.2 g of $\text{Ca}(\text{OH})_2$ were charged in a 4-necked reaction flask equipped as in Example 27. The temperature was raised to 170° C. followed by an addition of a further 0.1 g of $\text{Ca}(\text{OH})_2$. A vacuum of 30–40 mm Hg was thereafter applied and the temperature was raised to 230° C. The reaction was, under stirring, allowed to continue for 2 hours, after which time the acid value was determined to be 11.2 mg KOH/g. Obtained alkyd was, to remove suspended particles, finally filtered under pressure.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100%
Viscosity at 100° C.	620 mPas
Gardner colour value	5–6

EXAMPLE 35

An alkyd emulsion was prepared through emulsification in water of the alkyd according to Example 29. The emulsification was performed using a micro-fluidizer.

200.0 g of the alkyd according to Example 29 were charged in a double flanged vessel connected to an external water bath, in which vessel the alkyd was heated to 60° C. 12.0 g of a nonylphenolic emulsifier with an HLB-value of 16.0 were at 60° C. dissolved in 188.0 g of water. The water/emulsifier solution was, under heavy stirring by means of a high-speed dissolver, added to the alkyd. The thus formed emulsion was stirred for 5 minutes at 60° C. and 2000 rpm. In order to further reduce the particle size and form a stable emulsion, this was heated to 80° C. and was for 6 minutes (12 passages) allowed to pass through a micro-fluidizer holding a temperature of 80° C.

Obtained alkyd emulsion exhibited the following properties:

Nonvolatile content	50%
Average particle size	0.37 μm

EXAMPLE 36

The alkyd according to Example 30 was emulsified using the same procedure as disclosed in example 35, but with the following two differences:

- An emulsifier with an HLB-value of 17.2 was used.
- 8.0 g of the emulsifier were dissolved in 192.0 g of water.

Obtained alkyd emulsion exhibited the following properties:

Nonvolatile content	50%
Average particle size	0.41 μm

EXAMPLE 37

211.8 g of the polyester according to Example 28, 139.4 g (0.94 mole) of a mixture of capric and caprylic acid, 0.21 g (0.003 mole) of $\text{Ca}(\text{OH})_2$ and 3.0 g of xylene were charged in a 4-necked reaction flask equipped with a stirrer, nitrogen inlet, a cooler and a water-trap

18

(Dean-Stark). The temperature was during 2 hours raised to 200° C. The reaction was, under stirring, allowed to continue for 6 hours, after which time the acid value was determined to be 9.9 mg KOH/g.

Obtained product exhibited the following properties:

Nonvolatile content	91%
Viscosity at 23° C.	33600 mPas
Hydroxyl value	165 mg KOH/g
Theoretical hydroxyl value	158 mg KOH/g

EXAMPLE 38

450.0 g of the polyester according to Example 27, 242.0 g (1.64 mole) of a mixture of capric and caprylic acid, 0.45 g (0.006 mole) of $\text{Ca}(\text{OH})_2$ and 21.0 g of xylene were charged in a 4-necked reaction flask equipped as in Example 37. The temperature was during 1 hour raised to 200° C. The reaction was allowed to continue at 200° C. until an acid value of 8.3 mg KOH/g was reached.

Obtained product exhibited the following properties:

Nonvolatile content	92%
Viscosity at 23° C.	25200 mPas
Hydroxyl value	215 mg KOH/g
Theoretical hydroxyl value	208 mg KOH/g

EXAMPLE 39

100.0 g of the product according to Example 37, 24.5 g (0.34 mole) of acrylic acid, 150 ml of toluene, 100.0 mg of methyl hydroquinone, 30.0 mg of nitrobenzene and 1.0 g of methane sulphonic acid were charged in a 3-necked reaction flask equipped with a Teflon® lined magnetic stirrer, air inlet, a cooler and a water-trap (Dean-Stark). The reaction mixture was heated to 135° C. and refluxed for 2 hours. 20.0 (0.28 mole) of acrylic acid and 1.0 g of methane sulphonic acid were thereafter added and the reaction was allowed to continue at 135° C. for a further 4 hours. The reaction mixture was now cooled to room temperature and neutralised to pH 7 using a 5% aqueous solution of NaOH (\approx 250 ml). The resulting mixture separated into two phases, excess of acrylic acid, as sodium acrylate, being in the water-phase which was removed. Additional 250 ml of toluene were charged and the solution was washed with distilled water (3 \times 150 ml) followed by an addition of 20.0 g of active carbon and 10.0 g of a filter aid (Celite). The mixture was heated to 60° C. and after 30 minutes filtered under pressure. 20.0 mg of methyl hydroquinone were finally added to the product/toluene mixture, whereupon toluene was evaporated at 40°–50° C. and 20 mm Hg with a minor stream of air bubbling through the product.

Obtained polyester acrylate exhibited the following properties:

Nonvolatile content	99%
Viscosity at 23° C.	52000 mPas
Acid value	5.4 mg KOH/g

EXAMPLE 40

200.0 g of the product according to Example 38, 100.8 g (1.4 mole) of acrylic acid, 500 ml of toluene, 400.0 mg of methyl hydroquinone, 50.0 mg of nitrobenzene and 3.0 g of methane sulphonic acid were charged in a 3-necked reaction flask equipped as in Example 39. The reaction mixture was heated to 130° C. and refluxed for 5 hours, whereupon it was cooled to room temperature and neutralised to pH 7 using a 5% aqueous solution of NaOH (\approx 250 ml). The resulting mixture separated into two phases, excess of acrylic acid, as sodium acrylate, being in the water-phase which was removed. The solution was then washed with distilled water (3 \times 400 ml) followed by an addition of 50.0 g of active carbon and 50.0 g of a filter aid (Celite). The mixture was heated to 60° C. and after 30 minutes filtered under pressure. 40.0 mg of methyl hydroquinone were finally added to the product/toluene mixture, whereupon toluene was evaporated at 40°–50° C. and 20 mm Hg with a minor stream of air bubbling through the product.

Obtained polyester acrylate exhibited the following properties:

Nonvolatile content	98%
Viscosity at 23° C.	16600 mPas
Acid value	3.8 mg KOH/g

EXAMPLE 41

A polyester epoxy resin was prepared in 2 steps.

Step 1—200.0 g of the product according to Example 38, 200 ml of toluene and 0.2 g (0.002 mole) of sulphuric acid were charged in a 4-necked reaction flask equipped with a stirrer and a cooler. The temperature was raised to reflux (\approx 110° C.) followed by an addition of 68.8 g (0.74 mole) of 1-chloro-2,3-epoxy propane during 30 minutes. The reaction mixture was now refluxed for 6 hours, whereupon an additional amount of 2.0 g of sulphuric acid were added. The solution was now refluxed for a further 8 hours, after which time it was cooled to 50° C. An ethyl ether solution of BF₃ (50% BF₃) was thereafter added in an amount of 1.0 g and the temperature was raised to \approx 110° C. The reaction solution was refluxed for 2 hours and then cooled to room temperature.

A gas chromatographic analysis showed less than 0.1% of unreacted 1-chloro-2,3-epoxy propane and the intermediate polyester halohydrin was thus presumed to have been obtained.

Step 2—The reaction mixture from Step 1 above was heated to 50° C. and 116.3 g (0.41 mole) of Na₂SiO₃·9H₂O were added. The temperature was raised to reflux (\approx 90° C.) and the reaction mixture was allowed to reflux for 4 hours. The reaction mixture was then cooled to room temperature and in order to remove suspended particles filtered under pressure.

Toluene and water were evaporated at 50° C. and 20 mm Hg. Acetone was then added and the resulting solution was once again filtered under pressure followed by evaporation of acetone at 50° C. and 20 mm Hg.

Obtained polyester epoxy exhibited the following properties:

Nonvolatile content	98%
Viscosity at 23° C.	14000–15000 mPas
Epoxy equivalent weight (EEW-value)	935

The EEW-value of 935 indicates that approximately one third of the hydroxyl groups have been converted into epoxy groups.

EXAMPLE 42

200.0 g of the polyester according to Example 27, 259.8 g (0.92 mole) of tall oil fatty acid and 0.28 g of Ca(OH)₂ were charged in a 4-necked reaction flask equipped as in Example 37. The temperature was during 2 hours raised to 210° C. and the reaction was allowed to continue for 3 hours, after which time the acid value was determined to be 21.2 mg KOH/g.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100%
Viscosity at 23° C.	2000 mPas
Gardner colour value	6

EXAMPLE 43

70.6 g of the product according to Example 37, 16.5 g of a hexamethoxymethyl melamine resin (nonvolatile content 97.2%), 9.0 g of xylene, 3.9 g of isobutanol and 0.64 g of para-toluene sulphonic acid (50% in ethanol) were mixed.

Resulting lacquer exhibited the following properties:

Nonvolatile content	80%
Viscosity at 23° C.	1760 mPas

The lacquer was filtered and thereafter coated on glass panels at a filmthickness of 40 \pm 5 μ m (dry) and cured at 160° C. for 10, 20 and 30 minutes. The film hardness was by means of a König Pendulum determined after conditioning at 23 \pm 2° C. and 50 \pm 5 relative humidity.

The following results were obtained:

Curing Time at 160° C.	Pendulum Hardness König seconds
10	87
20	87
30	80

EXAMPLE 44

An acid curing lacquer was prepared having the following formulation:

Alkyd according to Example 42	28.22 g
Urea resin (nonvolatile content 74%)	15.04 g *1
Melamine resin (nonvolatile content 95%)	2.24 g *2
Ethanol	4.57 g
Nitrocellulose (nonvolatile content 26%)	17.57 g *3
Methoxy propanol	8.61 g
Butyl acetate	13.83 g

-continued

p-Toluene sulphonic acid (20% in ethanol)	5.56 g
*1 Dynomin U121E, Dyno Cyanamid K.S., Norway	
*2 Dynomin MB98, Dyno Cyanamid K.S., Norway	
*3 VF-1/2, Nobel Kemi AB, Sweden	

Resulting lacquer exhibited the following properties:

Nonvolatile content	51.9%
Viscosity at 23° C. (Ford Cup no. 4)	26 seconds

The lacquer was coated on glass panels at a filmthickness of $40 \pm 5 \mu\text{m}$ (dry) and cured at 23° C. and 60° C. The film hardness was by means of a König Pendulum determined after conditioning at $23 \pm 2^\circ \text{C}$. and $50 \pm 5\%$ relative humidity.

The following results were obtained:

	Pendulum Hardness König seconds
Curing Time at 23° C.	
30	11
60	17
120	24
140	31
Curing Time at 60° C.	
5	36
10	42
15	45
20	48
25	49

EXAMPLE 45

The following driers were mixed with products according to Examples 31-34:

Zirconium salt	0.25%
Cobalt salt	0.03%

Above percentages were calculated as 100% metal on the non-volatile content of the products.

An antiskin agent (Exkin 2, Servo B.V., The Netherlands) was, furthermore, added in an amount of 0.30%.

The thus prepared lacquers were coated on glass panels at a filmthickness of $50 \pm 5 \mu\text{m}$.

The drying time was measured as through dry using the thumb test method.

The results are given in Table 7.

EXAMPLE 46

The following watersoluble driers were mixed with alkyd emulsions according to Examples 35 and 36

Zirconium salt	0.25%*
Cobalt salt	0.20%*

*Servosyn Web, Servo Delden B.V., The Netherlands

Above percentages were calculated as 100% metal on the non-volatile content of the products.

An antiskin agent (Exkin 2, Servo B.V., The Netherlands) was, furthermore, added in an amount of 0.30%.

The thus prepared lacquers were coated on glass panels at a filmthickness of $40 \pm 5 \mu\text{m}$.

The drying time was measured as through dry using the thumb test method.

The results are given in Table 7.

EXAMPLE 47

UV-curing lacquers based on polyester acrylates according to Examples 39 and 40 were prepared having the following formulation:

Polyester acrylate acc. to Ex. 39 or 40	50.0 g
Tripropylene glycol diacrylate	25.0 g
Polyol TP 30 triacrylate	25.0 g *1
Photoinitiator	4.0 g *2

*1 Trifunctional acrylic monomer prepared from Polyol TP 30 (ethoxylated trimethylolpropane, Perstorp Polyols, Sweden) and acrylic acid. The monomer can be prepared according to known acrylation procedures.

*2 Darocur 1173, Firma E. Merck, Fed. Rep. of Germany

Lacquer based on polyester acrylate according to Ex. 39 had a viscosity of 480 mPas, while the viscosity of corresponding lacquer based on polyester acrylate according to Ex. 40 was 330 mPas. Both viscosities were determined at 23° C.

The lacquers were coated on glass and steel panels at a film-thickness of $30 \pm 5 \mu\text{m}$ (dry) and were UV-cured. UV-curing was performed using a Labcure Unit LC9 from Wallace Knight, UK, having a belt speed of 20 m/min. and an irradiation source consisting of medium pressure quartz mercury lamps of 80 Watts/cm.

The results are given in Table 6.

EXAMPLE 48

67.0 g (0.50 mole) of trimethylolpropane, 20.0 g of xylene and 0.67 g of an esterification catalyst (Fascat 4100, Atochem, The Netherlands) were charged in a 3-necked reaction flask equipped as in Example 39. The temperature was raised to 160° C. and 603.0 g (4.50 moles) of dimethylolpropionic acid was during 30 minutes added. The temperature was thereafter raised to 190° C. and the reaction was allowed to continue for 7 hours, after which time the acid value was determined to be 50.2 mg KOH/g.

The hydroxyl value of obtained polyester was 557 mg KOH/g, corresponding to a theoretical hydroxyl value of 572 mg KOH/g.

EXAMPLE 49

60.0 g of the polyester according to Example 48, 562.8 g (4.20 moles) of dimethylolpropionic acid, 380.0 g (1.33 mole) of tall oil fatty acid, 30.0 g of xylene and 1.0 g of an esterification catalyst (Fascat 4100, Atochem, The Netherlands) were charged in a 3-necked reaction flask equipped as in Example 39. The temperature was raised to 210° C. and the reaction was allowed to continue for 5 hours until an acid value of 6.3 mg KOH/g was reached. Additional 760.0 g (2.67 moles) of tall oil fatty acid was thereafter charged and the reaction was allowed to continue for another 11 hours, after which time the acid value was determined to be 6.7 mg KOH/g. Resulting alkyd was, to remove suspended particles, finally filtered under pressure at a temperature of 100° C.

Obtained alkyd exhibited the following properties:

Nonvolatile content	100%
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-continued

Viscosity at 23° C.

20200 mPas

EXAMPLE 50

The alkyd according to Example 49 was, by oxidation of double bonds, converted into an epoxy resin. The process involved a catalyst disclosed by Crivello, J. V.; Narayan, R. in Chem. Mater. 1992, 4, pages 692-699.

Preparation of Catalyst

Glacial acetic acid was to 40.0 g of an ion-exchange resin (Amberlite IR-120 plus, Rohm & Haas Co., USA) added in such an amount that the resin was immersed. The mixture was at room temperature stirred mechanically during 4-5 hours and was thereafter washed with 8×40 ml of acetone. The catalyst was ready for use after a drying time of 24 hours at room temperature.

Preparation of Epoxy Resin

20.0 g of the alkyd according to Example 49, 10.0 ml of toluene, 1.52 g of glacial acetic acid and 2.06 g of above catalyst were mixed and heated under mechanical stirring to 50° C. 6.73 g of hydrogen peroxide was added by drops. The temperature was during the peroxide addition not allowed to exceed 55° C. A large volume of toluene was after 12 hours added and the solution was filtered. An additional portion of toluene was thereafter added and the solution was several times dried with MgSO₄. Nonvolatile matters were finally evaporated using a rotary evaporator.

Obtained product was characterized through NMR and the degree of conversion of unsaturated bonds to epoxidized groups was determined to be 88%.

EXAMPLE 51

A hyperbranched polyester was prepared as a so called 9 generations dendrimer and the Mark-Houwink constant was determined.

The polyester synthesis was in 8 steps carried out in a flanged reaction flask equipped with argon inlet, a Teflon® lined magnetic stirrer, a drying tube and a junction to water suction. The reaction flask was placed in an oil bath holding a constant temperature of 150° C. Each of the 8 steps of the synthesis consisted of 2 hours of reaction with a stream of argon passing through the reaction mixture and 1 hour of reaction under vacuum.

The scheme of the synthesis was as follows and the reaction conditions as above:

Step 1: 0.0056 mole of trimethylolpropane, 0.05 mole of dimethylolpropionic acid and 0.34 g of para-toluene sulphonic acid were charged.

Step 2: 0.067 mole of dimethylolpropionic acid and 0.045 g of para-toluene sulphonic acid were added to the reaction product of step 1.

Step 3: 0.13 mole of dimethylolpropionic acid and 0.09 g of para-toluene sulphonic acid were added to the reaction mixture of step 2.

Step 4: 0.13 mole of dimethylolpropionic acid and 0.09 g of para-toluene sulphonic acid were added to 15.0 g of the reaction product of step 3.

Step 5: 0.13 mole of dimethylolpropionic acid and 0.09 g of para-toluene sulphonic acid were added to 15.0 g of the reaction product of step 4.

Step 6: 0.13 mole of dimethylolpropionic acid and 0.09 g of para-toluene sulphonic acid were added to 15.0 g of the reaction product of step 5.

Step 7: 0.13 mole of dimethylolpropionic acid and 0.09 g of para-toluene sulphonic acid were added to 15.0 g of the reaction product of step 6.

Step 8: 0.13 mole of dimethylolpropionic acid and 0.09 g of para-toluene sulphonic acid were added to 15.0 g of the reaction product of step 7.

The after the 8th reaction step thus obtained product was a 9 generations dendritic polyester having a theoretical molecular weight of 178000 g/mole.

The Mark-Houwink constant was for above polyester determined by means of a RALLS Laser-RI Viscosimetry Equipment* from Viskotek Inc., USA, which is a system consisting of a size exclusion chromatograph with 3 detectors in serial and computerised software processing of data.

* RALLS=Right Angel Laser Light Scattering RI=Refractive Index

6.0 mg of prepared dendritic polyester were dissolved in 1.0 ml of tetrahydrofuran and 100.0 µl of the solution were injected into above equipment.

The Mark-Houwink constant for above polyester was found to be $\alpha=0.23$, which value complies with corresponding theoretical value for a spherical macromolecule.

EXAMPLE 52

A polyurethane dispersion based on a dendritic polyester was prepared in 2 steps and evaluated in a lacquer formulation.

Step 1: 300.0 g of the polyester according to Example 27 were charged in a 4-necked reaction flask, equipped as in Example 27, and heated to 130° C. 98.6 g of propionic acid were thereafter during 15 minutes added and the reaction was allowed continue for 2.5 hours, giving an acid value of 11.9 mg KOH/g and a hydroxyl value of 276 mg KOH/g

Step 2: 73.0 g of the product obtained according to Step 1, 23.1 g of isophorone diisocyanate, 5.0 g of dimethylolpropionic acid, 20.0 mg of benzoyl chloride, 0.16 g of Sn(II)-octoate and 200 ml of acetone were charged in a 3-necked reaction flask equipped with a Teflon® lined magnetic stirrer, a cooler and a Dean-Stark separator. A water bath was used as heating device. The reaction mixture was during 8 hours refluxed at 58° C., whereupon an additional amount of 0.16 g of Sn(II)-octoate was added. The reaction was now allowed to continue for 5 hours, after which time 4.0 g of dimethylethanol amine and 126.0 g of water were added. Acetone was thereafter removed from the reaction mixture by distillation. Small amounts of dimethylethanol amine were during the distillation added in order to improve the solubility of the product in the water phase.

Obtained product, a transparent low viscous polyurethane dispersion, exhibited the following properties:

Nonvolatile content:	37.4%
Free NCO-content:	0.2%
NCO-conversion:	92%

Above polyurethane dispersion was mixed with a water soluble melamine resin (Cymel 327, Dyno Cyanamid K.S., Norway) forming a lacquer with the following formulation:

Polyurethane dispersion (as solid)	60% by weight
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-continued

Melamine resin (as solid)	40% by weight
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Prepared lacquer was coated on glass panels at a film thickness of $40 \pm 5 \mu\text{m}$ (dry) and cured at 160°C . The film hardness was after curing and conditioning at $23 \pm 2^\circ \text{C}$. and $50 \pm 5\%$ relative humidity determined by means of a König Pendulum.

A pendulum hardness of 180 König seconds was after 10 minutes of curing at 160°C . obtained.

TABLE 1

Example no.	1.	2.	3.	4.	5.	6.	7.
1	1.5	§	2637	3027	2322	1.30	10.0
2	1.5	§	1908	2045	1527	1.34	1037
3	1.5	All	3366	3513	2811	1.25	1.5
4	1	§	1686	2000	1638	1.22	3.9
5	1	All	2173	2000	1621	1.23	0.73
6	2	§	2588	4094	3142	1.30	18.4
7	2	All	4560	4406	3105	1.42	2.6

1. Moles charged dimethylolpropionic acid per mole hydroxyl groups from ditrimethylolpropane.
2. Hydroxyl groups, from product obtained in step 1, which have been further reacted with fatty acid in step 2.
3. Calculated molecular weight of the final product, as obtained after step 2, expressed in g/mole.
4. Molecular weight, M_n .
5. Molecular weight, M_w .
6. Dispersivity $H, M_w/M_n$.
7. Viscosity at 23°C . in Pas

TABLE 2

Example no.	8	9	10	11	12	13	14
Base polyol	DiTMP	DiTMP	DiTMP	DiTMP	TMP	—	—
Moles DMPA/mole base polyol	8	8	4	12	9	—	—
Hydroxyl groups from step 1 terminated in step 2	10/12	10/12	7/8	13/16	10/12	—	—
<u>Calculated Properties</u>							
Acid number, mg KOH/g	0	0	0	0	0	4.5	10
Hydroxyl number, mg KOH/g	32	35	22	34	30	32	63
Molecular weight, g/mole	3518	3208	2527	5009	3768	1860	4060
Oil length as triglyceride, %	82.3	72.2	80.2	75.2	76.9	82.2	61.8
<u>Determined Properties</u>							
Acid number, mg KOH/g	4.5	2.8	4.7	5.4	7.3	5.0	6.1
Hydroxyl number, mg KOH/g	21	32	26	21	20	42	—
Nonvolatile content, %	100	100	100	100	100	100	62.5
Viscosity at 23°C ., mPas	1160	2950	620	2060	1180	1900	2880
<u>Film Hardness, König seconds</u>							
5 hours drying	22	21	18	24	21	Tacky	8
8 hours drying	27	15	24	45	46	11	10
24 hours drying	76	36	69	73	63	24	10
<u>Drying Time, Beck-Koller</u>							
Dust dry, hours	3.0	2.3	3.3	2.0	2.0	3.0	1.5
Through dry, hours	4.5	13.0	6.8	4.2	4.6	>24	21.5

DiTMP = Ditrimethylolpropane
DMPA = Dimethylolpropionic acid
TMP = Trimethylolpropane

TABLE 3

Properties	Example no.	
	20	21
Viscosity at 23°C ., Pas	33	210
Nonvolatile content, %	100	100
Calculated molecular weight, g/mole	3490	3830
Analysed molecular weight M_n , g/mole	4000	4800
Analysed molecular weight M_w , g/mole	6400	18100
Dispersivity $H, M_w/M_n$	1.62	3.78

TABLE 4

Curing time at 80°C .	Pendulum hardness in König Seconds	
	Example 22	Example 23
20 minutes	14	119
30 minutes	58	144
40 minutes	75	160
50 minutes	86	161
60 minutes	96	167

TABLE 5

Number of passages under UV-lamps	Pendulum Hardness in König Seconds	
	Product acc. to Example 24	Product acc. to Example 24 mixed 50:50 with TPGDA
1 passage	122	Adhesive*
2 passages	153	—
3 passages	161	126
4 passages	165	133
5 passages	165	133
6 passages	—	139
7 passages	—	136
10 passages	170	—

TPGDA = Tripropylene glycol diacrylate
*Oxygen inhibition

TABLE 6

Number of passages under UV-lamps	Acrylate acc. to Example 39	Acrylate acc. to Example 40
-----------------------------------	-----------------------------	-----------------------------

Pendulum Hardness in König Seconds

1 passage	66	67
2 passages	77	80
4 passages	90	88
8 passages	106	111
16 passages	134	118
<u>Pencil Hardness</u>		
8 passages	B-HB	B-HB
<u>Erichsen Flexibility in mm</u>		
8 passages	3.1	3.4

TABLE 7

Example no.	31	32	33	34	35	36
Base polyol	PP 50	PP 50	PP 50	PP 50	PP 50	PP 50
Moles DMPA/mole base polyol	12	28	252	60	124	60
Hydroxyl groups from step 1 terminated in step 2	14/16	29/32	239/256	58/64	239/256	58/64
<u>Calculated Properties</u>						
Acid number, mg KOH/g	0	0	0	0	0	0
Hydroxyl number, mg KOH/g	16	15.9	15.8	15.8	15.8	15.8
Molecular weight, g/mole	5600	11300	91000	22700	91000	22700
Oil length as triglyceride, %	82.3	72.2	80.2	75.2	76.9	82.2
<u>Determined Properties</u>						
Acid number, mg KOH/g	8.2	9.4	9.5	11.2	9.5	11.2
Nonvolatile content, %	100	100	100	100	50*	50*
Viscosity at 23° C., mPas	1800	1400	43500	—	—	—
<u>Drying</u>						
Through dry, hours	5-6	3	2	2-3	6-7	7-8

PP 50 = Polyol PP 50 (ethoxylated pentaerythritol, Perstorp Polyols, Sweden)

*Alkyd emulsion

We claim:

1. A dendritic macromolecule wherein
 - (i) a central initiator molecule or initiator polymer having at least one reactive hydroxyl group (A), which hydroxyl group (A) under formation of an initial tree structure is bonded to a reactive carboxyl group (B) in a monomeric chain extender having the two reactive groups (A) and (B), which tree structure
 - (ii) optionally is extended and further branched from the initiator molecule or initiator polymer through an addition of further molecules of a monomeric chain extender by means of bonding with the reactive groups (A) and (B) thereof and
 - (iii) optionally is further extended through reaction with a chain stopper
 and wherein the monomeric chain extender has at least one carboxyl group (B) and at least two hydroxyl groups (A) or hydroxyalkyl substituted hydroxyl groups (A).
 2. The dendritic macromolecule according to claim 1 wherein the central initiator molecule or initiator polymer is selected from the group consisting of:
 - a) an aliphatic, a cycloaliphatic or an aromatic diol
 - b) a triol
 - c) a tetrol
 - d) a sugar alcohol
 - e) anhydroennea-heptitol or dipentaerythritol
 - f) an α -alkylglucoside
 - g) a monofunctional alcohol
 - h) an alkoxylate polymer having a molecular weight of at most 8000 and being produced by reaction between an alkylene oxide and one or more hydroxyl groups originating from compounds a) through g).
 3. The dendritic macromolecule according to claim 2 wherein said initiator molecule is selected from the group consisting of ditrimethylolpropane, ditrimethylolpropane, dipentaerythritol, pentaerythritol, alkoxylated pentaerythritol, trimethylolpropane, trimethylolpropane, alkoxyated trimethylolpropane, glycerol, neopentyl glycol, dimethylolpropane, 1,3-dioxane-5,5-dimethanol, sorbitol, mannitol and α -methylglucoside.
 4. The dendritic macromolecule according to claim 1 wherein the chain extender is selected from the group consisting of:
 - a) a monofunctional carboxylic acid having at least two hydroxyl groups
 - b) a monofunctional carboxylic acid having at least two hydroxyl groups wherein one or more of the hydroxyl groups are hydroxyalkyl substituted.
 5. The dendritic macromolecule according to claim 4 wherein said chain extender is selected from the group consisting of dimethylolpropionic acid, α,α -bis(hydroxymethyl)butyric acid, α,α,α -tris(hydroxymethyl)acetic acid, α,α -bis(hydroxymethyl)valeric acid, α,α -bis(hydroxy)propionic acid and 3,5-dihydroxybenzoic acid.
 6. The dendritic macromolecule according to claim 1 wherein said macromolecule is chain stopped and the chain stopper is selected from the group consisting of:
 - a) a saturated monofunctional carboxylic acid or a saturated fatty acid or an anhydride thereof
 - b) an unsaturated fatty acid
 - c) an unsaturated monofunctional carboxylic acid
 - d) a diisocyanate or an oligomer thereof
 - e) an adduct of a reaction product of a diisocyanate or an oligomer thereof
 - f) a difunctional or a polyfunctional carboxylic acid or an anhydride thereof
 - g) an adduct of a reaction product difunctional or a polyfunctional carboxylic acid or an anhydride thereof
 - h) an aromatic monofunctional carboxylic acid
 - i) an epihalohydrin
 - j) a glycidyl ester of a monofunctional carboxylic acid or of a fatty acid, which acid has 1-24 carbon atoms
 - k) an epoxide of an unsaturated fatty acid with 3-24 carbon atoms.
 7. The dendritic macromolecule according to claim 6 wherein said chain stopper is selected from the group consisting of lauric acid, linseed fatty acid, soybean fatty acid, tall oil fatty acid, dehydrated castor fatty acid, capric acid, caprylic acid, trimethylolpropane diallyl ether maleate, metacrylic acid, acrylic acid, benzoic acid, para-tert.butylbenzoic acid, 1-chloro-2,3-epoxy propane, 1,4-dichloro-2,3-epoxy butane and epoxidized soybean fatty acid.
 8. The dendritic macromolecule according to claim 1 wherein said macromolecule is chain stopped and wherein the chain extender is dimethylolpropionic acid and the initiator molecule is selected from the group consisting of ditrimethylolpropane, trimethylolpropane, ethoxylated pentaerythritol, pentaerythritol and glycerol.

9. A dendritic macromolecule according to claim 1 being a constituent in the preparation of a product selected from the group consisting of:

- a) an alkyd, an alkyd emulsion, a saturated polyester or an unsaturated polyester
- b) an epoxy resin
- c) a phenolic resin
- d) an amino resin
- e) a polyurethane resin, foam or elastomer
- f) a binder for radiation curing or powder systems
- g) an adhesive
- h) a synthetic lubricant
- i) a microlithographic paint
- j) a composite reinforced with glass, aramid or carbon/graphite fibres
- k) a moulding compound based on urea-formaldehyde resins, melamine-formaldehyde resins or phenol-formaldehyde resins
- l) a dental material.

10. A process of making a dendritic macromolecule according to claim 1 wherein said initiator molecule or initiator polymer is reacted with said chain extender at a temperature of 0°-300° C.

11. The process of according to claim 10 wherein said temperature is 100°-250° C.

12. The process of making a dendritic macromolecule according to claim 10 wherein a molar ratio between the chain extender and hydroxyl groups originating from the initiator molecule or the initiator polymer of 1:1 is 2000:1 is employed.

13. The process according to claim 12 wherein said molar ratio is 1:1 to 1100:1.

14. The process of making a dendritic macromolecule according to claim 10 wherein reaction water formed during the reaction is removed by means of inlet of an inert gas into the reaction vessel, by azeotropic distillation or by vacuum distillation.

15. The process according to claim 14 wherein said reaction water is continuously removed.

16. The process of making a dendritic macromolecule according to claim 10 wherein at least one esterification catalyst is present.

17. The process according to claim 16 wherein said catalyst is selected from the group consisting of:

- a) a Bronstedt acid
- b) a Lewis acid
- c) a titanate
- d) zinc powder or an organozinc compound
- e) tin powder or an organotin compound

18. The process according to claim 16 wherein said catalyst is selected from the group consisting of naphthalene sulphonic acid, p-toluene sulphonic acid, methane sulphonic acid, trifluoromethane sulphonic acid, trifluoroacetic acid, sulphuric acid, phosphoric acid, BF₃, AlCl₃, SnCl₄ and tetrabutyl titanate.

19. The process of making a dendritic macromolecule according to claim 10 wherein the central initiator molecule or initiator polymer is selected from the group consisting of:

- a) an aliphatic, a cycloaliphatic or an aromatic diol
- b) a triol
- c) a tetrol
- d) a sugar alcohol
- e) anhydroennea-heptitol or dipentaerythritol
- f) an α -alkylglucoside
- g) a monofunctional alcohol

h) an alkoxylate polymer having a molecular weight of at most 8000 and being produced by reaction between an alkylene oxide thereof and one or more hydroxyl groups originating from compounds a) through g).

20. The process according to claim 19 wherein said initiator molecule is selected from the group consisting of ditrimethylolpropane, ditrimethylolethane, dipentaerythritol, pentaerythritol, alkoxylated pentaerythritol, trimethylolethane, trimethylolpropane, alkoxylated trimethylolpropane, glycerol, neopentyl glycol, dimethylolpropane, 1,3-dioxane-5,5-dimethanol, sorbitol, mannitol and α -methylglucoside.

21. The process of making a dendritic macromolecule according to claim 10 wherein the chain extender is selected from the group consisting of:

- a) a monofunctional carboxylic acid having at least two hydroxyl groups
- b) a monofunctional carboxylic acid having at least two hydroxyl groups wherein one or more of the hydroxyl groups are hydroxyalkyl substituted.

22. The process according to claim 1 wherein said chain extender is selected from the group consisting of dimethylolpropionic acid, α,α -bis(hydroxymethyl)-butyric acid, α,α,α -tris(hydroxymethyl)-acetic acid, α,α -bis(hydroxymethyl)valeric acid, α,α -bis(hydroxy)-propionic acid and/or 3,5-dihydroxybenzoic acid.

23. The process of making a dendritic macromolecule according to claim 10 wherein said macromolecule is chain stopped and the chain stopper is selected from the group consisting of:

- a) a saturated monofunctional carboxylic acid or a saturated fatty acid or an anhydride thereof
- b) an unsaturated fatty acid
- c) an unsaturated monofunctional carboxylic acid
- d) a diisocyanate or an oligomer thereof
- e) an adduct of a reaction product a diisocyanate or an oligomer thereof
- f) a difunctional or a polyfunctional carboxylic acid or an anhydride thereof
- g) an adduct of a reaction product of a difunctional or a polyfunctional carboxylic acid or an anhydride thereof
- h) an aromatic monofunctional carboxylic acid
- i) an epihalohydrin
- j) a glycidyl ester of a monofunctional carboxylic acid or of a fatty acid, which acid has 1-24 carbon atoms
- k) an epoxide of an unsaturated fatty acid with 3-24 carbon atoms.

24. The process according to claim 23 wherein said chain stopper is selected from the group consisting of lauric acid, linseed fatty acid, soybean fatty acid, tall oil fatty acid, dehydrated castor fatty acid, capric acid, caprylic acid, trimethylolpropane diallyl ether maleate, metacrylic acid, acrylic acid, benzoic acid or para-tert. butylbenzoic acid, 1-chloro-2,3-epoxy propane, 1,4-dichloro-2,3-epoxy butane and epoxidized soybean fatty acid.

25. The process of making a dendritic macromolecule according to claim 10 wherein said macromolecule is chain stopped and wherein the chain extender is dimethylolpropionic acid and the initiator molecule is selected from the group consisting of ditrimethylolpropane, trimethylolpropane, ethoxylated pentaerythritol, pentaerythritol and glycerol.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,418,301
DATED : May 23, 1995
INVENTOR(S) : Anders Hult, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1, line 8: delete "composed of"
Column 2, line 20: delete "an"
Column 9, lines 17 & 34: "mpas" should read
--mPas--
Column 12, line 36: "35°" should read --35--
Column 15, line 61: "27,938.0" should read
--27, 938.0--
Column 18, line 18: "27,242.0" should read
--27, 242.0--
Column 21, line 28: "140" should read --240--
Column 23, line 2: "mpas" should read --mPas--
Column 23, line 54: "0,067" should read --0.067--
Column 23, line 55: "0,045" should read --0.045--
Column 28, line 43, Claim 6: after "product" insert
--of a--
Column 30, line 3: delete "thereof"
Column 30, line 37, Claim 23: after "product" insert
--of--

Signed and Sealed this
Eighteenth Day of June, 1996

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

Introduction to dendritic macromolecules

Dendritic polymers are highly branched macromolecules with tree-like architectures, constructed from multifunctional monomers. Unlike conventionally branched polymers, (i.e. linear polymers containing branching units, dendritic polymers are capable of branching at each and every monomer repeat unit. This results in a large number of functionalised end groups. The branched nature of such structures also influences solution properties, reducing hydrodynamic volume and lowering solution viscosity compared to linear polymers. This unique combination of properties has led to dendritic polymers, being investigated for numerous applications including mechanical property modifiers,^{5,6} solution phase supports,^{7,8} non-linear optics,⁹ nanocomposites^{10,11} biomimetics¹²⁻¹⁴ and in medical applications such as drug and gene delivery.^{14,15} There are two main types of dendritic architecture, dendrimeric and hyperbranched. These structures are distinguished by the way in which they are branched. Dendrimeric structures display perfect branching and layered growth. In contrast, hyperbranched polymers (HBP) have less ordered structures, undergoing random growth with a proportion of branching opportunities remaining unfulfilled. This results in an imperfect less well-defined structure. Figure 1 shows these differences schematically for an AB_2 polymer, in which A groups react exclusively with B groups. In addition to exhibiting a randomly or perfectly branched structure, dendritic polymers can either be constructed entirely from monomer units or be attached to a central core. For perfectly branched dendrimeric polymers these two types of sub-structure are classified as dendrons and dendrimers respectively. Dendrons can be reacted with a multifunctional core to form a dendrimer. Interestingly, no such formal distinction exists for hyperbranched polymers although analogous structures are common.

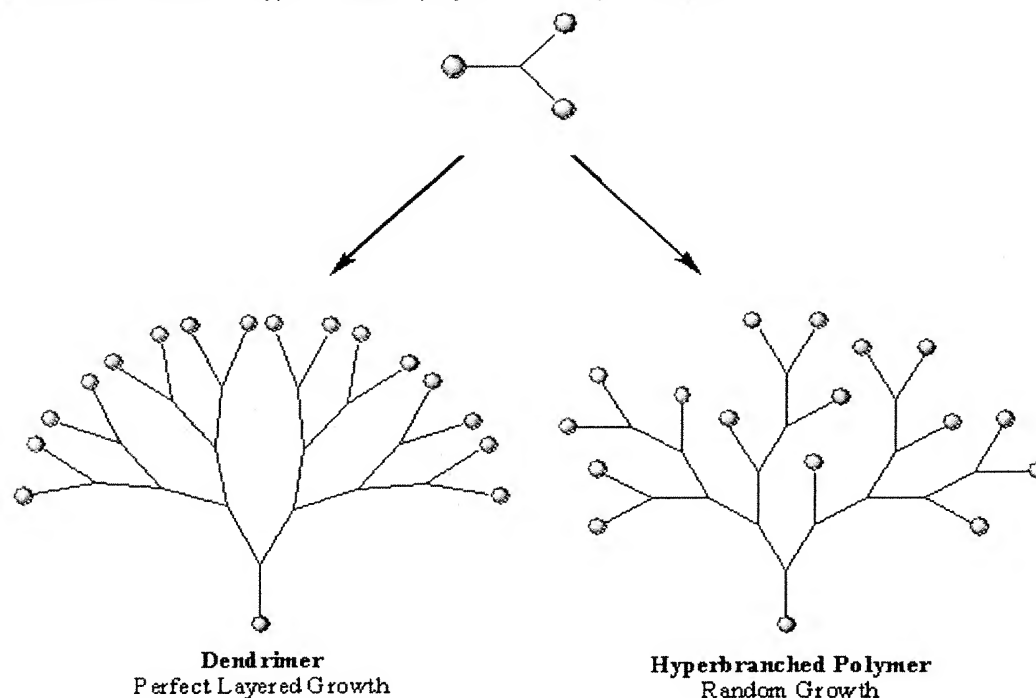


Figure 1 (above). Dendritic vs. Random Growth

As a result of their unique structure and properties many possible and important applications have been postulated for both dendrimers and HBP. These have included catalysis, imaging, and molecular machines, and indeed some of these applications are beginning to be realised.¹⁶ At Sheffield we are synthesising and studying a variety of dendritic macromolecules for a number of applications, these include;

- Dendritic polymers as enzyme mimics

- Dendrimers as size selective inhibitors to protein-protein binding
- Dendritic macromolecules as a potential artificial blood product
- Light harvesting dendritic polymers
- Immobilized Dendrons
- Solid phase applications
- Dendrimers and hyperbranched polymers for drug and gene delivery

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This work forms part of Lance Twyman's group research portfolio. For more research conducted by this group:

Lance Twyman's research



US006632889B1

(12) **United States Patent**
Yin et al.

(10) Patent No.: **US 6,632,889 B1**
(45) Date of Patent: **Oct. 14, 2003**

(54) **CONVERGENT SELF-BRANCHING
POLYMERIZATION**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/365,609**

(22) Filed: **Aug. 2, 1999**

Related U.S. Application Data

(63) Continuation of application No. PCT/US98/02838, filed on Feb. 17, 1998.

(60) Provisional application No. 60/038,727, filed on Feb. 18, 1997.

(51) Int. Cl.⁷ **C08J 271/02**

(52) U.S. Cl. **525/279; 525/280; 525/417**

(58) Field of Search **525/274, 280, 525/417**

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(57) ABSTRACT

A method of forming a branched polymer includes forming a plurality of growing linear polymer chains by polymerizing a monomer which is protected against branching and which forms a reactive end group which is in a first condition which is one of electrophilic or nucleophilic, exposing the growing linear polymer chains to a chain transfer agent to cause the reactive end group of at least a first growing linear polymer chain to reverse its electrophilic or nucleophilic character, whereby a non-reversed reactive end group on a second growing linear polymer chain reacts with the reversed reactive end group on the first growing linear polymer chain to create a branched polymer and reverses the electrophilic or nucleophilic character of the reversed reactive end group back to its first condition, whereby it may continue adding monomer in a linear fashion; and quenching the polymerization by adding a compound having multiple reactive sites capable of reacting with the reactive end groups of the polymer chains when they are in the first condition. The method allows the preparation of ultra-high molecular weight dendritic polymers in which the branching junctures are assembled in situ (i.e., are self-branching) in a convergent manner during polymerization of the monomers.

8 Claims, 3 Drawing Sheets

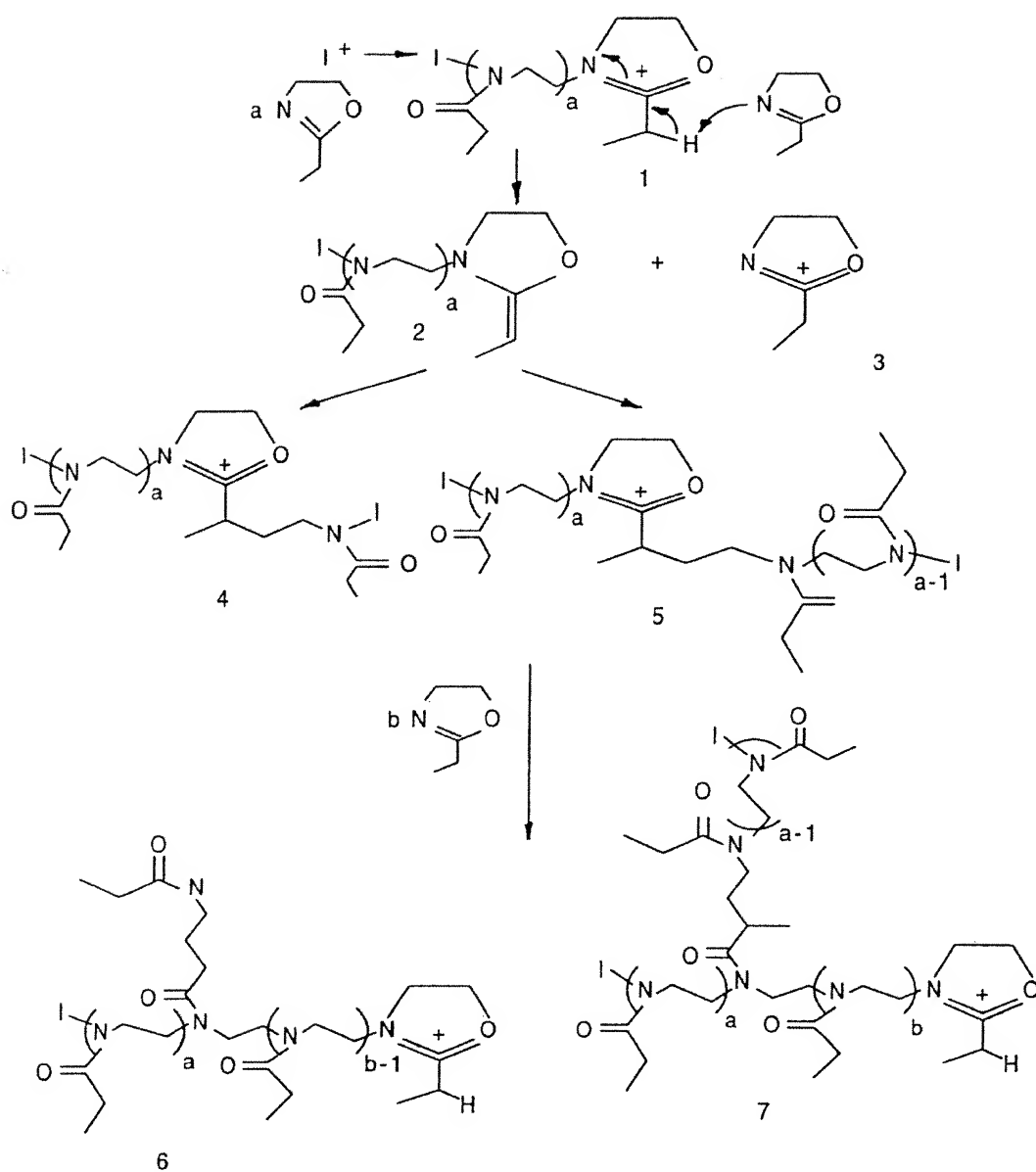
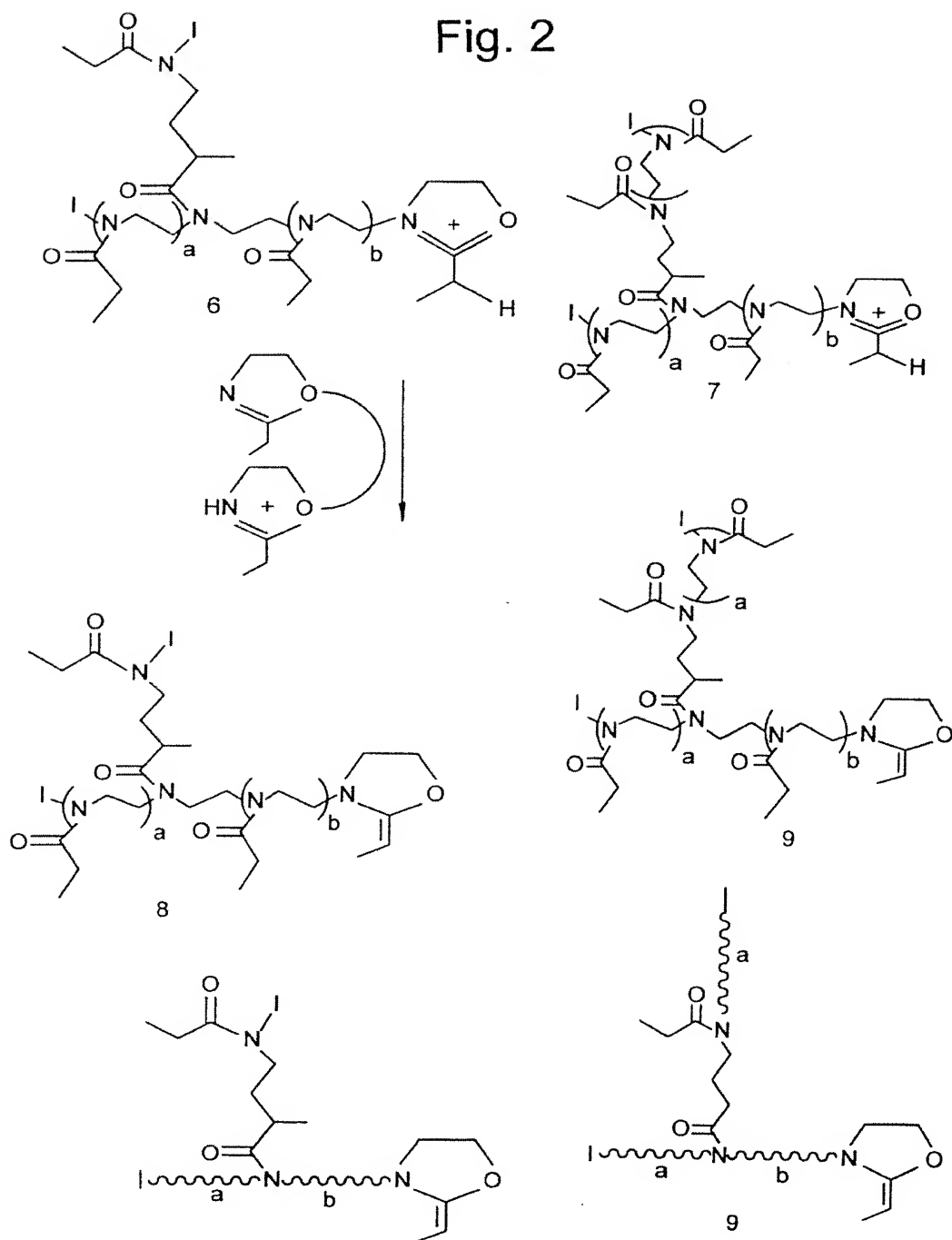
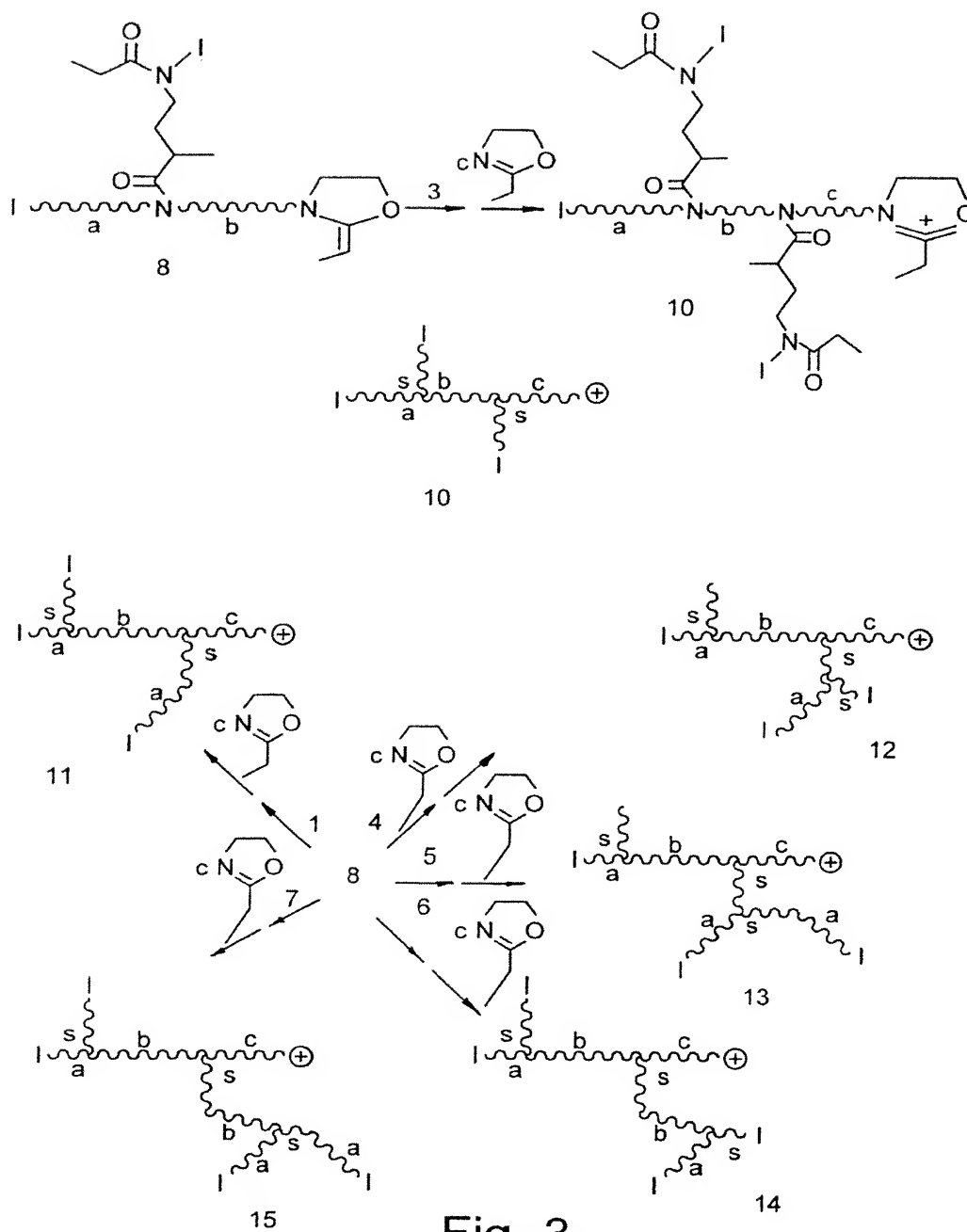


Fig. 1

Fig. 2





CONVERGENT SELF-BRANCHING POLYMERIZATION

CLAIM OF PRIORITY

This is a continuation of PCT Application No. PCT/US98/02838, filed Feb. 17, 1998, which claims priority to U.S. Provisional Application No. 60/038,727, filed Feb. 18, 1997, to each of which this application claims priority.

FIELD OF THE INVENTION

This invention relates generally to polymerization of branched polymers, and, more particularly, to a method of preparing very high molecular weight branched polymers and to the resulting high molecular weight branched polymers.

BACKGROUND OF THE INVENTION

Since the first dendrimer synthesis was reported in mid 1980's, dendritic polymers including dendrons, dendrimers, dendrigrafts, and random hyper-branched polymers have quickly been recognized as the fourth major molecular architecture, which exhibits very different properties over the traditional linear, branched, and crosslinked polymers. For example, the dendritic polymers possess smaller sizes, lower viscosities, higher number of surface functional groups, faster reaction kinetics, and controlled interior void spaces when compared with their linear counterparts. The well defined dendrons, dendrimers, and dendrigrafts are normally prepared through a stepwise synthetic process, which often makes them too expensive to be utilized in most of the industrial applications. The cheaper dendrimer analogs, random hyper-branched polymers, have mostly been prepared through polycondensation of AB_x monomers (x is 2 or greater). However, due to difficulties associated with condensation reactions, the molecular weights (MWs) of these polymers were generally low, and new monomer syntheses were often required. Very recently, Fréchet and his coworkers have developed a self-condensing vinyl polymerization approach, in which an AB monomer having both an initiating center and a propagating center was utilized to produce random hyper-branched polymers. Since each AB monomer has an initiating center, a large amount of initiators (equivalent to monomers) had to be utilized in this polymerization.

SUMMARY OF THE INVENTION

This invention pertains to a method of preparing ultra-high molecular weight dendritic polymers in which the branching junctures are assembled in situ (i.e., are self-branching) in a convergent manner during polymerization of the monomers. The invention also relates to dendritic polymers prepared in accordance with the method.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1-3 are reaction schemes showing the convergent self-branching polymerization of ethyloxazoline.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with one aspect of the invention, a method of forming a branched polymer capable of achieving high molecular weight comprises polymerizing a monomer which is protected against branching and which forms a reactive end group which is in a first electrophilic or

nucleophilic condition. The monomer, at least during a portion of the polymerization reaction, is susceptible of reversing its electrophilic or nucleophilic character (i.e., from electrophilic to nucleophilic or from nucleophilic to electrophilic) by reaction with a chain transfer agent. The growing linear polymer chains are exposed to a chain transfer agent so that the reactive end group of a growing linear polymer chain reverses its electrophilic or nucleophilic character. Thereafter, a non-reversed reactive end group on a second growing linear polymer chain reacts with the reversed reactive end group on the first growing linear polymer chain to create a branched polymer. During this reaction wherein the non-reversed reactive end group of a second growing linear polymer reacts with the reversed reactive end group of a first growing linear polymer, the electrophilic or nucleophilic character of the reversed reactive end group is again reversed back to its first condition. Upon being reversed to its original condition, the end group which was originally part of the first growing polymer chain reacts with a monomer from which linear polymerization proceeds. Thereafter, the resulting branched polymers having an electrophilic or nucleophilic end group are reacted with a compound having multiple reactive sites capable of reacting with the reactive end groups of the polymer chains when they are in the first condition, whereby a branched polymer is formed from a monomer which is protected against branching.

In accordance with another aspect of the invention, a composition of matter comprising a branched polymer prepared by the method of this invention is provided.

This invention provides a new approach to the production of ultra-high MW dendritic polymers in which the branching junctures are assembled in situ (self-branching) through a convergent manner during the polymerization of commercially available monomers. We term this polymerization as convergent self-branching polymerization (CSBP). In contrast to the polycondensation of AB_x monomers, in which interior branching junctures have been previously built in the monomers, the self-branching polymerization generates branching junctures during the propagation of monomers. Similar to the synthesis of Starburst® dendrimers, these branching junctures can be constructed through both divergent and convergent approaches. The divergent self-branching polymerization (DSBP) amplifies its reactive chain ends and allows them to branch from an inside core to outside terminal groups, while the convergent self-branching polymerization combines the reactive chain ends and allows them to branch from the outside terminal groups to the inside core. The best example for DSBP is Fréchet's self-condensing vinyl polymerization, in which both an initiating center and a propagating center were present in each AB monomer, and the branching junctures were generated through simultaneous and continuous initiating and propagating processes during the polymerization. In the case of CSBP, in addition to chain propagation, a chain branching reaction also occurs during the polymerization. For example, a chain transfer reaction (from an active chain end to a monomer) may generate a macromonomer, as well as another new active chain end. This macromonomer can then be combined with this new or another active chain end to generate a dimer-like molecule with a new active chain end in the middle of the polymer chain. The resulting chain ends can further propagate with more monomers and then combine with another macromonomer to form a Y-shape branched molecule with a newly generated reactive chain end at the focal point. This newly generated reactive chain end can again propagate with more monomers and then

combine with another macromonomer to form a hyper-branched polymer with its reactive chain end at the focal point. This process will repeat again and again during the polymerization until the chain end is terminated. If the terminating moiety is a monofunctional core molecule, a dendron-like hyper-branched polymer will be formed. If a multifunctional or dendrimer core is utilized, a dendrimer-like, spherical hyper-branched polymer will be generated. Similarly, if a multifunctional linear polymeric core is used, a dendrigraft-like hyper-branched polymer will also be obtained.

A fundamental difference between traditional linear polymerization and a self-branching polymerization is that the former prefers one reaction pathway (i.e., propagation), while the latter undergoes two or more reaction pathways (i.e., propagation and branching). For example, in a traditional vinyl or ring-opening polymerization process, one reaction pathway (i.e., initiation and propagation) is often preferred in order to produce pure linear polymers. However, in reality, it is very difficult to control the polymerization condition, which only allows the desired reaction pathway to occur. In most cases, there are always some side reactions occurred during the polymerization processes, which generate undesired side products such as pre-terminated low molecular weight linear polymers, cyclic polymers, chain transfer polymers, and branched polymers. If the undesired "side reaction" (i.e., premature termination and cyclization) can be suppressed and the desired "side reactions" (i.e., chain transfer and branching) can be promoted in addition to polymer chain propagation, the conventional polymerization processes which were widely used to produce one dimensional linear polymer could also be utilized to prepare three dimensional tree-like polymers.

As a particular example, the invention will be illustrated with reference to the convergent self-branching polymerization of ethyloxazoline.

With reference to FIG. 1, a cationic initiator, such as a carbonium ion is contacted with ethyloxazoline to form a growing linear chain having an end group which is electrophilic. This growing linear chain having an electrophilic end group is designated by the number 1 in the reaction scheme. At some point during the polymerization process, a chain transfer agent (in this case the monomer itself) reacts with the growing chain to form a linear polyethyloxazoline chain having a nucleophilic end group (represented by the compound designated by the number 2 in the reaction scheme). The nucleophilic linear polymeric chain (compound 2 in the reaction scheme) can react with the electrophilic linear polymer chain (compound 1 in the reaction scheme) to form a compound (compound 5 in the reaction scheme) having an electrophilic reactive moiety bounded to two linear polymeric chains, and with the electrophilic moiety serving as a site for additional polymerization of a polymeric branch. In particular, compound 5 in the reaction scheme can be reacted with additional monomer to form a branched polymer (the compound designed number 7 in the reaction scheme) having one branch with a reactive, electrophilic terminal. In accordance with an alternative pathway, compound 2 can be reacted with the protenated monomer (compound 3) to form compound 4 in the reaction scheme. Compound 4 in the reaction scheme can be reacted with additional monomer to form a polymer (compound 6) having a reactive, electrophilic end group.

With reference to FIG. 2, polymers 6 and 7 can be reacted with additional monomer to form polymers 8 and 9 which can be represented in either of two alternative schematic formulas illustrated in the reaction scheme. As shown in

FIG. 3, polymer 8 can be reacted with additional monomer or additional monomer and one of compounds 4, 5, 6 or 7 to form polymers 11, 12, 13, 14 and 15 respectively.

The various polymeric compounds formed in the above reaction scheme can be reacted with (i.e., quenched with) any of various compounds having multiple reactive sites capable of reacting with the reactive end groups of the various polymer chains. For example, in the case of the polyethyloxazoline compounds (e.g., compounds 7-14) can be contacted with a linear polyethyleneimine having a plurality of nucleophilic reactive sites which can combine with the polyethyloxazoline compounds having electrophilic sites. The compound having multiple reactive sites capable of reacting with the reactive end groups on the polymer chains can be of generally any molecular architecture. For example, in the case of the polyethyleneimine compounds the polyethyleneimine can be linear, including rigid rods, and cyclic or closed linear polymers; cross-linked polymers, including lightly cross-linked polymers, densely cross-linked polymers, and interpenetrating networks; branched polymers, including random short branched polymers, random long branched polymers, regular comb-branched polymers and regular star-branched polymers; or dendritic polymers, including random hyper-branched dendritic polymers, dendrigrafts, dendrons, and dendrimers.

Synthesis of New Dendritic Polymers

Using the method of this invention, polymers having a molecular weight of 1,000,000 or above can be prepared. For example, a hyper-branched polymer having a linear polyethyleneimine core with a plurality of branched polyethyloxazoline moieties grafted thereto can be prepared in accordance with this invention having a molecular weight of at least 1,000,000.

The convergent self-branching polymers of this invention can be advantageously employed in various applications including: Ag/Pharma Delivery, Lubrication, Adhesives, Rapid Cure Coatings, Composites, Crosslinking Agents, Metal Chelation, Gene Transfection, Diagnostic Assays, MRI Agents, Water Treatment, Environmental Remediation (Clean-up), Paper Finishing Chemicals, Viscosity Modifiers, Antistatic Agents, Ceramic Fabrication, Polymer Additives, Ink-jet Printing, Photographic Reagents, Reprography reagents, Chromatography Supports/Ion Exchange Resins and Electrophoretic Gels.

EXAMPLES

Methyl p-toluenesulfonate, p-toluenesulfonic acid, morpholine, and diisopropylethylamine were purchased from Aldrich. 2-Ethyloxazoline was obtained from Monsanto. Toluene, methylene chloride, diethyl ether, and methanol were purchased from Fisher. Methyl p-toluenesulfonate was purified by vacuum distillation, while 2-ethyloxazoline, morpholine, diisopropylethylamine toluene, and methylene chloride were stirred over CaH_2 and distilled prior to use.

Synthesis of Hyper-Branched Polyethyloxazoline Polymers [HBP(500-20)]

The synthesis of hyper-branched polyethyloxazoline [HBP(500-20)] is provided as a general procedure for the preparation of hyper-branched polymers. A mixture of p-toluene sulfonic acid (1.92 g, 0.01009 mol) in 500 ml of toluene was azeotroped to remove water with a distillation head under N_2 for about 15 min. After cooling to about 60° C., 2-ethyloxazoline (500 g, 5.045 mol) was added dropwise

through an addition funnel, and the mixture was allowed to reflux between 6 and 24 hours. To this mixture was added a linear polyethylenimine core (0.015 mol of NH, 1.5 eq), which was dried by azeotropic distillation from toluene, followed by immediate addition of diisopropylethylamine (2 eq). The mixture was refluxed for 2 hours, cooled, and the top toluene layer was decanted off. The crude product was redissolved in methanol and then precipitated out from a large excess of diethyl ether. The bottom layer was redissolved in methanol and dried by rotary evaporation and vacuum to give a PEOX hyper-branched polymer as a white solid (~500 g, MW>1,000,000, Tg~40° C.). Other hyper-branched polymers such as HBP (250-20), HBP (250-50), HBP (250-100), HBP (250-500), HBP (500-20), HBP (500-50), HBP (500-500), HBP 750-20), HBP (750-50), HBP (750-100), HBP (1000-100), HBP (2000-100), and HBP (5000-100) etc. could be prepared in a similar manner. All the products were analyzed by SEC, NMR, DSC, and TGA.

Synthesis of Hyper-Branched PEI Polymers, PEI (500-20)

To a round bottom flask was added 40 g of HBP (500-20), 20 g of concentrated H₂SO₄ (98 wt %), and 200 ml of deionized water. The mixture was refluxed for 6 hours, and then neutralized by NaOH until pH is around 10-11. After rotary evaporation of water, the crude product was redissolved in methanol, and then filtered through a Buchner funnel. The filtrate was rotary evaporated to remove methanol, and the residue was redissolved in methylene chloride and then filtered through a Buchner funnel. The filtrate was rotary evaporated and then dried by vacuum to give a hyper-branched PEI polymer, PEI(500-20)-NH₂ as white gum (MW>500,000 Tg—2° C.).

What is claimed is:

1. A method for forming a branched polyethyloxazoline or polyethyleneimine polymer capable of achieving high molecular weights comprising:

forming a plurality of growing linear polymer chains by polymerizing, as a monomer, 2-ethyloxazoline which is protected against branching and which forms a reactive end group, upon contact with a carbonium ion, which is in a first condition which is electrophilic, and which at least during a portion of the polymerization reaction is susceptible of reversing its electrophilic character to

nucleophilic by reaction with more of said monomer functioning as a chain transfer agent;

exposing the growing linear polymer chains to the chain transfer agent to cause the reactive end group of at least a first growing linear polymer chain to reverse its electrophilic character, whereby a non-reversed reactive end group on a second growing linear polymer chain reacts with said reversed reactive end group on said first growing linear polymer chain to create a branched polymer, and reverses said nucleophilic character of said revised reactive end group back to its first condition of electrophilic character, whereby it may continue adding monomer in a linear fashion; and quenching the polymerization by adding polyethyleneimine capable of reacting with said reactive end groups of said polymer chains when they are in said first condition of electrophilic character, whereby a branched polymer is formed from said monomer which is protected against branching.

2. The method of claim 1 in which said monomer is selected such that the linear polymer chains which it forms grow to degrees of polymerization in excess of about 100 before the electrophilic character of said reactive end groups is capable of being reversed by exposure to remaining monomer units acting as chain transfer agents.

3. The method of claim 1 in which said chain transfer agents are not introduced into said reaction vessel until after the polymerization has been allowed to proceed for a time sufficient to yield linear polymer chains of a desired degree of polymerization.

4. The method of claim 1 in which said compound having multiple reactive sites comprises one or more of the group consisting of linear polymers, branched polymers, cross-linked polymers, and dendritic polymers.

5. A composition of matter comprising a polymer prepared by the method of claim 1.

6. The composition of claim 5 having a molecular weight of about 1,000,000 or above.

7. The composition of claim 5 wherein the polymer is polyethyloxazoline.

8. The composition of claim 5 wherein the polymer is polyethyleneimine.

* * * * *

**SYNTHESIS AND
CHARACTERIZATION OF
ARYLMETHYL SULFONE
DENDRIMERS AND
HYPERBRANCHED
POLY(PHENYLENE
SULFIDE)/POLY(SULFONE)**

By

Qiuxia (Lucy) Zhao

This manuscript has been read and accepted by the Graduate Faculty in the department of Chemistry and Biochemistry at Seton Hall University in satisfaction of the dissertation requirement for the Degree of Doctor of Philosophy.

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Table of Contents

Abstract	1
Acknowledgements.....	4
Introduction	
General background for polymers.....	6
Background of dendritic polymers.....	13
Background of hyperbranched polymers.....	26
Background of polysulfones/polysulfides.....	30
Reference.....	36
Part 1: synthesis of sulfone dendrimers	
Introduction.....	45
Result and Discussion.....	50
Conclusion.....	62
Experiment.....	62
Schemes.....	68
Tables.....	91
Figures.....	93
Reference.....	118
Part 2: synthesis and characterization of hyperbranched polyphenylene sulfide and sulfone	
Introduction.....	121
Results and Discussion.....	125
Conclusion.....	138
Experiment.....	139
Schemes.....	143
Tables.....	152
Figures.....	156
Reference.....	170

Abstract

Synthesis and Characterization of Arylmethyl Sulfone Dendrimers and Hyperbranched Poly(phenylene sulfide) / Poly(phenylene sulfone)

By

Qiuxia(Lucy) Zhao

Adviser: Dr. James E. Hanson

In recent years, nonlinear polymers such as dendritic and hyperbranched macromolecules have attracted considerable attention owing to the potential new properties of their highly branched, highly functionalized, three-dimensional globular structures. Chemists have begun to explore controlled ways of making synthetic polymers with highly branched structures, known as dendrimers and hyperbranched polymers. Dendrimers have a well-defined and perfectly branching structure, and are built up by either a stepwise divergent or convergent approach. Hyperbranched polymers are prepared by a one-step polymerization process that yields a highly branched, irregular structure.

A synthetic approach to an arylmethyl sulfone dendrimer was explored based on a convergent synthesis. An A_2B monomer with activated A sites and protected B site is required, and 5-sulfo-isophthalic acid sodium salt was used as a starting material. First, two carboxylic acids at the A sites were protected by esterification in methanol/concentrated sulfuric acid, then the sulfonic acid at the B site was protected by making a sulfonate ester via the sulfonyl

chloride. Second, two A sites were activated by reducing the esters to benzyl alcohols, then transforming to benzyl chlorides to generate the phenyl 3,5 – bis - chloromethyl - benzenesulfonate monomer. Following a common method for synthesis of sulfones, this monomer was reacted with benzenesulfinic acid sodium salt to make a generation I (G1) arylmethyl sulfone dendrimer. The deprotection of the phenylbenzenesulfonate was not successful. Literature methods such as decomposition with hydrazine and reduction all failed.

Hyperbranched poly(phenylene sulfide) was prepared from 3,5-dichlorobenzenethiol by one-pot approach using K_2CO_3 as base, NMP as solvent, and 150 °C for 8 hours. Hyperbranched poly(phenylene sulfone) was generated by oxidization with H_2O_2 from hyperbranched poly(phenylene sulfide). A core-terminated hyperbranched poly(phenylene sulfide) was prepared by adding 1,3,5-trichlorobenzene as a core under the same conditions. An end-capped hyperbranched poly(phenylene sulfide) was made by adding 2-naphthalenethiol as an end-cap. The polymers were primarily characterized by size exclusion chromatography with light scattering detection (which provided the molecular weights and distributions) and thermal methods such as differential scanning calorimetry/thermogravimetric analysis. Polymerization for 8 hours at 150 °C in NMP gave hyperbranched poly(phenylene sulfide) with an M_w of 29 kD and a polydispersity of 1.1; core-terminated hyperbranched poly(phenylene sulfide) with an M_w of 14 kD and a polydispersity of 1.1 and end-capped hyperbranched poly (phenylene-sulfide) an M_w of 18 kD and a

polydispersity of 1.2. Hyperbranched poly-(phenylene sulfide), core-terminated hyperbranched poly(phenylene sulfide), end-capped hyperbranched poly(phenylene sulfide) and hyperbranched poly(phenylene sulfone) were amorphous with T_g of 74, 66, 75 and 203 °C respectively and no apparent crystallinity by differential scanning calorimetry (DSC). Thermogravimetric analysis(TGA) showed that the materials were very thermally stable, with decomposition temperatures between 375 and 545 °C in both air and N_2 atmospheres.

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I would like to thank my mentor, Dr. James E. Hanson, for his tutelage and guidance during my eight years at Seton Hall University. I learned a lot from him in organic chemistry, physical chemistry, and polymer chemistry.

I would like to thank the faculty at the Department of Chemistry and Biochemistry at Seton Hall University for their help and encouragement.

I would also like to thank Seton Hall University for financial support.

Introduction

General background of polymers

Polymers are large molecules – macromolecules made of repeating units. The small repeating molecules used as the basic building blocks for those large molecules are known as monomers. The name is derived from the Greek *poly*, meaning “many”, and *mer*, meaning “part”. There is no clear cut boundary between polymer chemistry and organic chemistry. Generally, if the relative molar mass of the molecule is at least 1000 or the number of repeat units in the molecule is at least 100, the molecule is considered to fall into the domain of polymer chemistry.¹

J.J. Berzelius, a famous Swedish chemist, was the first person to use ‘polymer’ as a scientific term in 1827.² But while almost a century elapsed, no one understood polymers. In 1920, Herman Staudinger published his famous paper on the structure of macromolecules. In this and subsequent papers, he argued that, “in high polymers many single molecules are held together by normal valency bonds. The tendency to form such compounds is observed in particular in organic chemistry due to the special nature of carbon”.³ After a decade of controversy, these ideas began to be accepted widely. Staudinger was awarded the Nobel Prize in 1953 for his work on polymers. By the 1930s, Carothers used esterification and amidation, well-established reactions of organic chemistry, to synthesize polymers. Physical chemists, such as, Kuhn, Cuth and Mark also began to describe the multitude of forms that a long-chain molecule could assume by statistics and crystallography.⁴

Today, polymer science has had a major impact on the way we live.⁵ It is very hard to find an aspect of our lives that is not affected by polymers. Polymeric materials are used in nearly all areas of daily life. Certain polymers, such as DNA, RNA, protein, starch, cellulose, and silk, are found in nature, while many others, including styrene-butadiene rubber, plastics, and fibers, are produced only by synthetic routes.

Natural rubber, obtained from the bark of the rubber tree, has been used by humans for many centuries. In 1823, Charles Goodyear succeeded in “Vulcanizing” natural rubber by heating it with sulfur so that rubber became valuable material. Today, the United States consumes on the order of a million tons of synthetic rubber, called styrene-butadiene rubber each year.

Among the most important and versatile of the hundreds of commercial plastics is polyethylene. Polyethylene is used in a wide variety of applications because, based on its structure, it can be produced in many different forms. The first type to be commercially exploited was low density polyethylene (LDPE). This polymer is characterized by a large degree of branching, forcing the molecules to be packed rather loosely forming a low density material. LDPE is soft and pliable and has applications ranging from plastic bags, containers, textiles, and electrical insulation, to coatings for packaging materials. Another form of polyethylene, differing from LDPE only in structure, is high density polyethylene (HDPE) or linear polyethylene. This form demonstrates little or no branching, enabling the molecules to be tightly packed. HDPE is much more rigid

than branched polyethylene and is used in applications where rigidity is important. Major uses of HDPE are plastic tubing, bottles, and bottle caps.

Natural fibers such as cotton, wool, and silk have been used by humans for many centuries. In 1885, artificial silk was patented and launched the modern fiber industry. Man-made fibers include materials such as nylon, polyester, rayon, and acrylic. Synthetic fibers have been developed that possess desirable characteristics, such as a high softening point to allow for ironing, high tensile strength, adequate stiffness, and desirable fabric qualities. These polymers are then formed into fibers with various characteristics.

Nylons (polyamides) were developed in the 1930s. They have special properties which distinguish them from other materials. One such property is elasticity. Nylon is very elastic, however after the elastic limit has been exceeded the material will not return to its original shape. Like other synthetic fibers, Nylon has a large electrical resistance.

A number of polymers are used in medical application.¹ For examples, poly(methyl methacrylate) can be supplied for hard and soft contact lenses, bone cement for artificial joints; poly(hydroxyethyl methacrylate) can be used in soft contact lenses and burn dressings.

Polymer-based medicines have been produced for the diagnosis and treatment of cancer and other diseases.⁶ Poly(ethylene glycol)-chemotherapy (e.g. doxorubicin, paclitaxel, camptothecins) conjugation promotes tumor targeting through the enhanced permeability and retention time and, at the cellular level following endocytic capture, allows lysosomotropic drug delivery.

The future for polymer chemistry appears limitless. The current journals in the field are filled with reports on new types of polymers and improvements in known polymers, together with articles dealing with better methods of characterizing polymers.

There are a number of methods of classifying polymers.⁷ Based on polymers' thermal processing behavior, they can be divided into thermoplastics and thermosets. Those polymers that can be heat-softened in order to process into a desired form are called thermoplastics. Polyethylene, polypropylene, poly(vinyl chloride) and polystyrene are major examples of commercial thermoplastics that can be recovered and refabricated by application of heat and pressure. On the other hand, those polymers where the individual chains have been chemically linked by covalent bonds during polymerization or by subsequent chemical or thermal treatment during fabrication and cannot be thermally processed are called thermosets. Those include epoxies and phenol-formaldehyde resins. Based on polymerization processes, polymers have been classified into addition polymers and condensation polymers. This classification, first proposed by Carothers,⁸ is based on whether the repeating unit of the polymer contains the same atoms as the monomer.

In addition-type polymers, the following applies:

1. The repeat unit in the polymer and the monomer have the same composition, although, of course, the bonding is different in each.

2. The mechanism of polymerization places addition polymerizations in the kinetic category of chain reactions, with either free radicals or ionic groups responsible for propagating the chain reaction.
3. The product molecules usually have a carbon chain backbone, with pendant substituent groups.

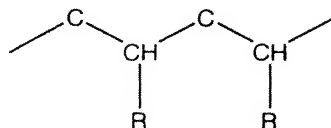


Table 1 illustrates some important vinyl polymers formed by addition polymerization.⁹

Table 1. Some Addition Vinyl Polymers

R	Common Name	Repeating unit
Cl	vinyl chloride	$\text{*-(CH}_2\text{---CHCl)-*}$
C ₆ H ₅	styrene	$\text{*-(CH}_2\text{---CH(C}_6\text{H}_5\text{))-*}$
CH ₃	propylene	$\text{*-(CH}_2\text{---CH(CH}_3\text{))-*}$
CN	acrylonitrile	$\text{*-(CH}_2\text{---CH(CN))-*}$
CONH ₂	acrylamide	$\text{*-(CH}_2\text{---CH(CONH}_2\text{))-*}$
COOH	acrylic acid	$\text{*-(CH}_2\text{---CH(COOH))-*}$

In condensation-type polymers:

1. The polymer repeat unit arises from reacting together two different functional groups which usually originate on different monomers. In this case, the repeat unit is different from either of the monomers. In addition, small molecules are often eliminated during the condensation reaction.
2. The reactions occur in steps.
3. The product molecules have the functional groups formed by the condensation reactions interspersed regularly along the backbone of the polymer molecules:



Some important commercial polymers are formed by condensation polymerization (Table 2).

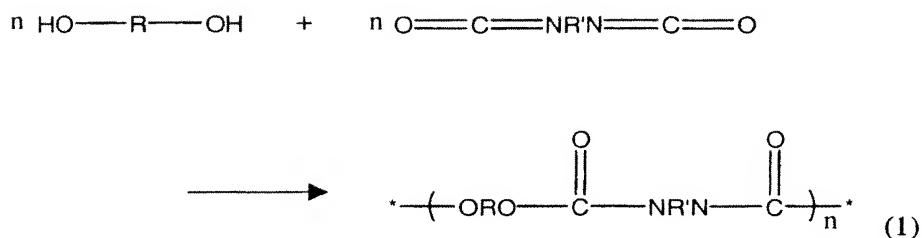
Table 2. Some Commercial Condensation Polymers

Polymer	Monomers	Repeating unit	Eliminated
Polycarbonate ester			HCl
polysulfide			NaCl
silicone rubber			HCl
polysulfone			NaCl

This addition-condensation system was slightly modified by P. J. Flory, who placed the emphasis on the mechanisms of the polymerization reactions. He reclassified polymerizations as step reactions or chain reactions.¹⁰

Step-reaction:

If the polymer chains are built up in a stepwise by the random union of monomer molecules to form dimers, trimers, and higher species throughout the monomer matrix, the process is called step-reaction polymerization. Equation 1 is a good example to show the formation of polyurethanes through step-reaction mechanism.



Chain-reaction:

If the polymer chains are propagated by adding one monomer molecule at a time, the process is called chain-reaction polymerization. Chain-reaction polymerization involves three steps, initiation, propagation and termination, for example, preparation of polyethylene (equation 2).

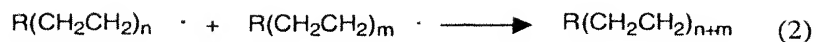
Initiation:



Propagation:



Termination:



In terms of molecular structure, polymers can be classified as linear, branched, dendritic, and hyperbranched (Figure1). A linear polymer has no branching other than the pendant groups associated with the monomer. A branched polymer is formed when there are 'side chains' attached to a main chain. Polymers with a high degree of branching are called dendrimers or hyperbranched polymers. But the differences between dendritic and hyperbranched are that dendritic branches have an exact number of concentric layers of branching points, on the other hand, hyperbranched branches have no exact number of concentric layers of branching points.⁹

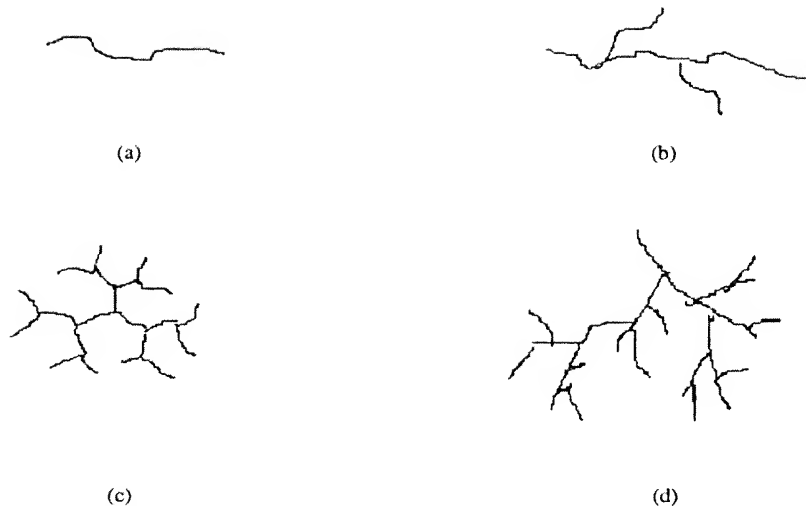


Figure 1. Representation of (a) linear polymer; (b) branched polymer; (c) dendrimer; (d) hyperbranched.

Background of dendritic polymers

The name dendrimer is derived from Greek words *dendron* meaning “tree” and *meros* meaning “part”. A major difference between linear polymers and dendrimers is that a linear polymer consists of long chains of molecules, like coils, crisscrossing each other. A dendrimer consists of molecular chains that branched out from a central core, and there is no entanglement between dendrimer molecules. Jean M. J. Frechet gave a lovely illustration for comparison of linear polymers and dendrimers is “cooked spaghetti” and “green peas”, respectively. The former is heavily entangled, but the latter is clearly not.¹¹

Dendrimers are perfectly cascade-branched, highly defined macromolecules, characterized by a combination of high end-group functionality and compact

molecular structures. Because of dendrimers' unique architecture, they have very unusual physical and chemical properties.^{12,13,14} As the molecular weight increases within a homologous series of dendrimers, the molecules undergo a transition from an extended to a globular shape. This transition is readily observed in a plot of intrinsic viscosity versus molecular weight (Figure 2). For linear polymers, the viscosity increases sharply with molecular weight (Figure 3). In a solubility test with THF as the solvent, the solubility of the dendritic polyester was found to be remarkably high, reaching 1.15 g/mL compared with 0.025 g/mL for the analogous linear polyester (the two polymers with molecular weight near 11,000).^{15,16} A marked difference in chemical reactivity was also observed in the catalytic hydrogenolysis of both polyesters with hydrogen gas and a solid Pd/C catalyst. Only the dendritic polyester was debenzylated, whereas the linear polyester was unreactive under a variety of reaction conditions.

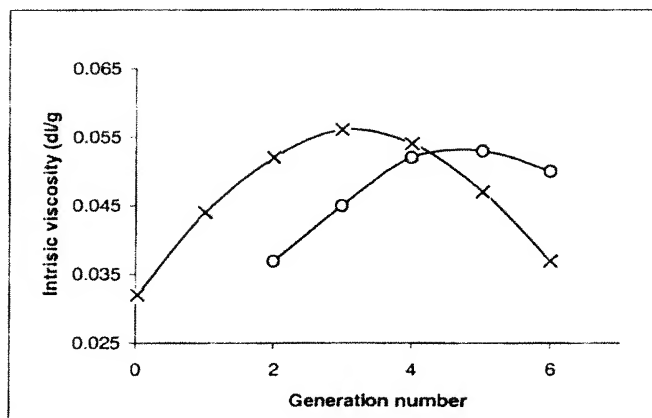


Figure 2. Plot of intrinsic viscosity versus generation number for polyether dendrimers x: Tridendron on core; o: Monodendron.

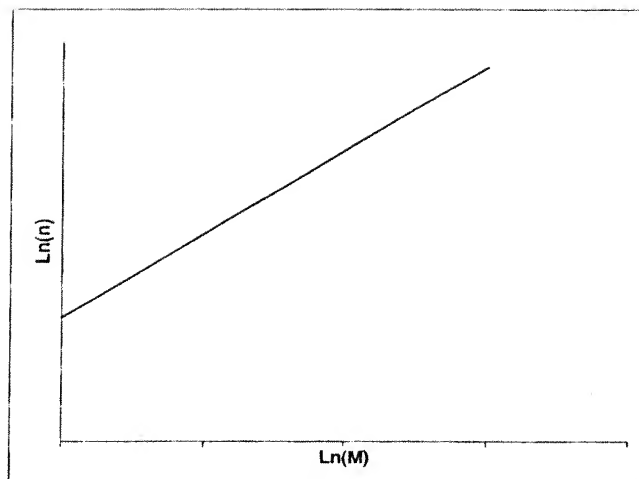


Figure 3. Mark-Houwink-Sakurada Equation: $\ln[n] = \ln(K) + a \ln(M)$
 n : intrinsic viscosity; M : molecular weight; K & a : constants.

Dendritic topologies can be observed everywhere on earth, for example, in abiotic systems, lightning patterns, snow crystals and tributary/erosion fractals; in biological systems, tree branching/roots, plant/animal vasculatory systems and neurons,¹⁷ but synthetic dendritic materials are a recent development. It was not until the mid-1980s that methods for the orderly preparation of these polymers had been sufficiently developed to enable their practical study. In 1978, Vogtle developed an iterative cascade method for the synthesis of low molecular weight branched amines.¹⁸ This was followed closely by the parallel and independent development of the divergent, macromolecular synthesis of “true dendrimers” in the Tomalia group.^{19,20} Tomalia et al synthesized and characterized the first family of dendrimers called poly(amidoamine) (PAMAM) in 1984-1985. The synthesis was initiated by Michael addition of three molecules of methyl acrylate to a “core” molecule of ammonia, followed by exhaustive amidation of the triester

adduct using a large excess of ethylenediamine, a process that generates a molecule with three terminal amine groups. Iterative growth is then continued using alternating Michael addition and amidation steps with the appropriate excess of reagents. Optimization of this procedure enabled the synthesis of globular PAMAM dendrimers on a commercial scale with molecular weights well above 25,000. Shortly thereafter, in 1985, Newkome reported preliminary results toward another family of tribranched polyamide dendrimers²¹ and in 1993, improvements on the original Vogle synthesis were disclosed by Meijer and Mulhaupt that enabled the true poly(propyleneimine) dendrimers.^{22,23} The route developed by Meijer is particularly notable because it also constitutes a viable commercial route to this family of aliphatic amine dendrimers.¹⁷ In 1989-1990, Hawker and Frechet developed the “convergent” methodology for dendrimer synthesis.^{24,25} The convergent growth approach, first demonstrated with poly(ether) dendrimers, is probably best described as an “organic chemist’s” approach to globular macromolecules because it affords outstanding control over growth, structure, and functionality. Up to date, convergent dendrons are probably the purest synthetic macromolecules prepared. Following these pioneering works, studies on dendrimers increased exponentially (Figure 4).

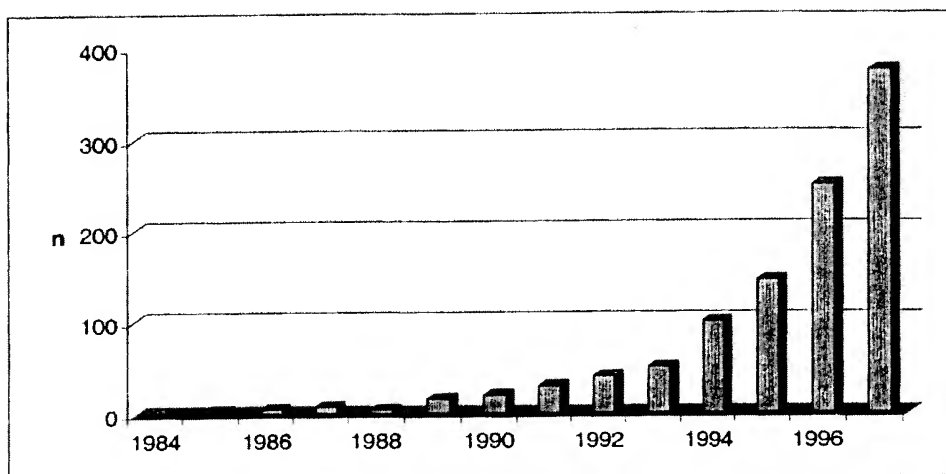


Figure 4. Number n of publications on dendrimers obtained from a CAS online search.

Due to dendrimers' unique physical and chemical properties, dendrimers have a wide range of potential applications.

1. Medicine and Diagnosis^{26, 27}

Dendrimers have been studied extensively as antitumor, antiviral, and antibacterial drugs. For example, poly(lysine) dendrimers modified with sulfonated naphthyl groups have been found to prevent/reduce transmission of HIV and other sexually transmitted diseases.²⁸ It is the first time a dendrimer pharmaceutical has been tested in humans. In earlier studies, it was found that PAMAM dendrimers covalently modified with naphthyl sulfonate residues on the surface, also exhibited antiviral activity against HIV. This dendrimer-based nano-drug inhibited early stage virus/cell adsorption and later stage viral replication by interfering with reverse transcriptase and/or integrase enzyme activities.²⁹

Dendrimers as hosts have been utilized to trap a variety of small molecules in their cavities. The trapped molecules can not diffuse out of the “dendritic box” until the box is opened enzymatically or photochemically.³⁰ Malik et al encapsulated the well-known anticancer drug cisplatin within PAMAM dendrimers to obtain conjugates that exhibited slower release, higher accumulation in solid tumors, and lower toxicity compared to free cisplatin.³¹

Dendrimers have been applied therapeutically in gene therapy as well.³² “Vectors” are employed to exchange a defective gene by a functioning one by the transfer of the genes through the cell membrane into the nucleus. Experiments showed that PAMAM-dendrimers are efficient transfection reagents and guarantee the transfer of genetic material into mammalian cells.³³ The use of dendritic structures for diagnostic purposes is also based on the possibility of multiplying certain functionalities and hence achieving higher sensitivities. Dendrimers have made crucial advances and have already been tested in preclinical studies, particularly in the field of contrast media for magnetic resonance. Magnetic resonance imaging (MRI) is a powerful technique in modern medical diagnostics and is used to visualize soft tissue. MRI is based on subtle differences of environment-sensitive ^1H NMR resonance (mainly of H_2O) in living systems, and can be enhanced by the administration of a paramagnetic contrast agent. The most widely approved contrast agents are currently Gd^{III} complexes in use but a major drawback is that these contrast agents rapidly diffuse into the extracellular matrix and consequently eliminate rapidly from the blood circuit.³⁴ As early as 1990, Lauterbur, Wiener and Tomalia pioneered the

use of dendrimer-based MRI contrast agents. Animal tests showed that dendrimer-based Gd^{III} chelates consisting of generations 2 and 6 PAMAM dendrimers with 12 and 192 terminal surface amines conjugated to the chelating ligand 2-(4-isothiocyanatobenzyl)-6-methyldiethylenetriaminepentaacetic acid through a thiourea linkage exhibited excellent MRI images of blood vessels upon intravenous injection and lasted sufficiently long in the blood circulation, with more than 100 minutes for large dendrimer(G=6) conjugates.³⁵

2. Nano Structures

An international focus is now emerging on nanotechnology. A very significant challenge facing the nanotechnology movement will be the development of structure-controlled methodologies that will enable cost-effective, controlled assembly of nanostructures in a routine manner.³⁶ Dendritic strategies allow the systematic construction of nanoscale structures and devices with precise atom-by-atom control as a function of size, shape, and surface chemistry. In the middle of 1990s, several groups, such as Frechet, Diederich, Tomalia, Percec et al, succeeded in preparing the nanometer-sized particles by using dendrimers.^{37, 38, 39, 40, 41}

3. Surface Coating

The peculiarities of dendritic structures offer new possibilities to manipulate the properties of surfaces by coating them.⁴² In the formation of dendrimers at interfacial areas, either gas-water or gas-solid transitions, a change in conformation compared to that in solution has been noticed. Its extent depends on the strength of the respective interactions. The stronger the attractive forces, the

more flattened the spherical shape becomes and the more it resembles a disc, so that for higher generations of elliptical PAMAM dendrimers an axial ratio of 1:3-6 has been observed.

To examine the sensory properties of such surfaces Crooks et al covalently linked PAMAM dendrimers to the carboxylic groups of a self-assembling monolayer(SAM) of sulfanylundecanoic acid on a gold surface.⁴³ They found on the basis of acoustic wave mass balances that dosing this modified surface with volatile organic compounds gave the essential attributes for an ideal chemical sensor. Immediately after the addition, an answer was detected which was reversible and showed a high signal-to-noise ratio. Furthermore, the sensor material guaranteed a differentiation between acids, alcohols and hydrophobic substances by the signal intensity. In addition it was noted that PAMAM dendrimers can be irreversibly attached to gold surfaces even without covalent binding. A complete, pH-selective distinction between cations and anions has been achieved by a new ultrathin multiplayer structure formed from an amphoteric polymer with covalently bound PAMAM dendrimers.⁴⁴ At low pH values these mixed membranes were permeable exclusively to anions, whereas in high pH-value regions only cations could pass.

4. Catalysis and Reaction Sites

Catalysis is one of the most promising applications in dendrimer research. Dendrimers have nanoscopic cavities that act like microenvironment for molecular reactions.⁴⁵ The cavities provide nanoscale reactor sites for catalysis because the core and surface of dendrimers are two catalytic sites. Bolm et al had

developed a dendrimer catalysis for enantioselective reduction of benzaldehyde.⁴⁶ The dendritic cavities provide a confined environment around the catalytic core and inducing regio and shape selectivity. The first peripheral catalytic site has been reported by Ford et al.⁴⁷

5. Combinatorial Chemistry

The idea of using dendrimers as a homogeneous soluble carrier for combinatorial libraries has been developed by Kim et al⁴⁸ to produce a small substance collection, based on Fischer's indole synthesis, with modified PAMAM dendrimers as carrier substances. Therefore they successively employed three N-protected amino acids, three keto carboxylic acids, and three hydrazine derivatives in a split synthesis. The more reasonable ratio of carrier material used to substance yield and the possibility of permanently controlling the reaction by spectroscopic methods is advantageous compared with the solid-phase synthesis. An automation of this process is also possible.

The unique physical and chemical properties of dendrimers have demonstrated great versatilities in variety of applications. The dendritic architecture challenges the creativity and the inventiveness of the chemists of all branches-from inorganic and organic chemistry, polymer and material chemistry, as well as analytical chemistry, biochemistry, to medicinal diagnosis.⁴⁹

Two complementary general approaches-divergent and convergent-have been used for the synthesis of dendrimers.^{50, 51} These were discussed briefly in the historical treatment, but a more formal description is given here.

- Divergent Approach

The divergent growth approach was the first method for dendrimer synthesis reported independently by Tomalia's group and Newkome's group in 1985. In the divergent method dendrimers are built stepwise from a small polyfunctional core through the reiteration of coupling and activation steps (Figure 5). The dendrimer can be built up step by step until steric effects prevent further reactions on the end groups.

The divergent process involves 4 steps:⁵² (1) Start with an initiator core possessing N_c reactive sites. (2) Choose a reaction sequence so that each of the N_c reactive sites adds a reactant B possessing N_b ($N_b \geq 1$) new reactive sites, which introduce multiplicity, to obtain dendrimer with generation 0. (3) Use protection/deprotection strategies to ensure that B reacts with all reactive sites of the core, but that no reactions occur at the new sites on B of dendrimer with generation 0. (4) Define an iterative sequence involving addition of new reactant B_i to the dendrimer D_i of generation i to form a new dendrimer D_{i+1} of generation $i+1$.

Both N_c (initiator-core multiplicity) and N_b (branch juncture multiplicity) directly affect the number of terminal groups (N), the number of repeating units (degree of polymerization DP), the number of dendrimer branch layers (N_{BL}), and the molar mass of the dendrimers as a function of generation (M). These values can be predicted mathematically for ideal system according to the following equations (3-6):

$$N = N_c N_b^G \text{ (G is the number of generation)} \quad (3)$$

$$DP = N_c (N_b^{G+1} - 1) / (N_b - 1) \quad (4)$$

$$N_{BL} = (N_b^G - 1) / (N_b - 1) \quad (5)$$

$$M = M_c + N_c [M_{RU} (N_b^{G+1} - 1) / (N_b - 1) + M_t N_b^{G+1}] \quad (6)$$

M_c : molar mass of initiator core
 M_{RU} : molar mass of repeat units
 M_t : molar mass of terminal units

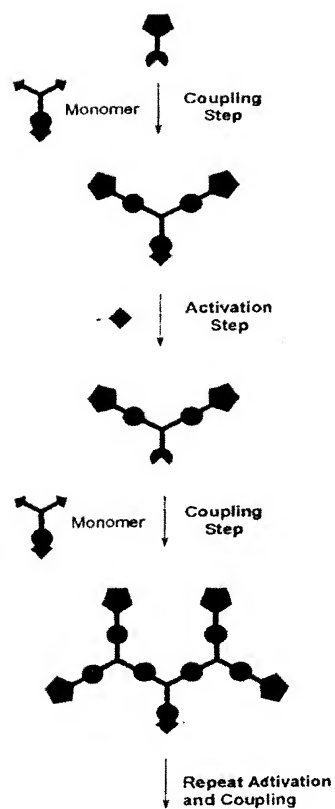
The best known representatives, poly(aminoamine) (PAMAM) dendrimers and poly(propyleneimine) dendrimers, are produced in kilogram scale by the divergent method.²⁰ One of the great advantages of this method is the ability to modify the surface of the dendrimer molecule. By changing the end groups at the outermost generation, the overall chemical and physical properties of the dendrimer can be configured to specific needs. Also the molecular weight and size of the dendrimer grow rapidly by the divergent method compared with the convergent one at the same number of reactions. Given an appropriate choice of coupling and activation steps, reagents, and reaction conditions, the divergent approach is ideally suited for the large-scale preparation of dendrimers. However, because the number of coupling reactions increase exponentially with each generation, the likelihood of incomplete functionalization or side reactions increase exponentially as well. Although removal of the monomer may be straightforward, any other flawed molecules resulting from incomplete reactions cannot be easily removed due to their structural similarity to the intended product. Hence, higher generations of divergently built-up dendrimers always contain certain structural defects.⁵³

- Convergent Approach

The convergent method, first reported by Hawker and Frechet in 1989-1990^{24,51}, initiates growth from what will eventually become the exterior of the molecule (Figure 5), and progresses inward by coupling end groups to each branch of the monomer. After completion of the coupling, the single functional group located at the focal point of the wedge-shaped dendritic fragment, or dendron, can be activated. Coupling of this activated dendron to each of the complementary functionalities on an additional monomer unit affords a higher generation dendron. After sufficient repetition of this process, these dendrons can be attached to a polyfunctional core through their focal point to form a globular multidendron dendrimer. The convergent route involves only a small number of reactions per molecule during the coupling and activation steps so that the reaction can be driven to completion with only a slight excess of reagent. Product purification after the coupling step employs the effective use of chromatography.

The convergent approach provides not only a single molecular species of precise molecular weight and structure but also extensive use in the construction functional macromolecules because of its ability to modify dendrons at both the focal point and the chain ends.⁵⁴ In addition, structural variations involving the attachment of chemically different dendrons to a single monomer unit are possible.⁵⁵ However, because the convergent synthesis is less readily scaled up than the divergent synthesis, its commercialization is presently limited to one family of polyether dendrons by Tokyo Kasei Co., Ltd. in Japan.²⁵

Convergent



Divergent

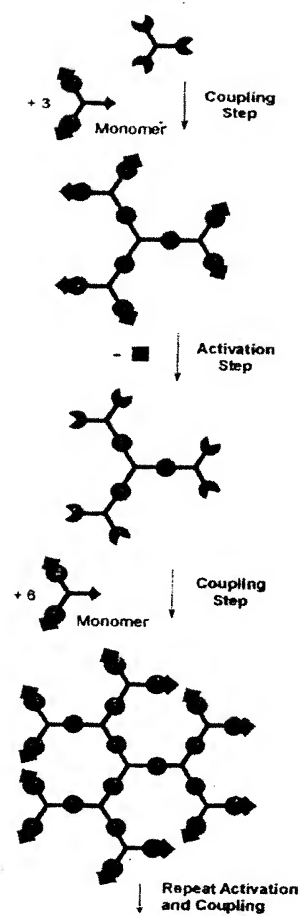


Figure 5. Convergent and divergent approach
(ref. chemical reviews, 2001, Vol. 101, No.12, 3821).

Background of hyperbranched polymers

Hyperbranched polymers are highly branched macromolecules with three-dimensional dendritic architectures. Hyperbranched polymers are related to dendrimers in that they exhibit dendritic branching but the branches do not emanate from a central core. In another word, dendrimers are differentiated from hyperbranched polymers by structural perfection, leading to an exact number of concentric layers of branching points.^{56,57,58,59} The comparison between hyperbranched polymers and dendrimers is shown in Table 3. In contrast to the iterative sequence of reaction and purification steps associated with dendrimer syntheses, the single step polymerization of AB_x ($x > 1$) monomers leads to hyperbranched structures. These materials, which are accessible at lower cost than their monodisperse dendrimer analogues, retain some of the structural features and properties of dendrimers and are consequently commercially attractive.⁶⁰

Table 3. Comparison between Hyperbranched Polymer and Dendrimer

	Hyperbranched Polymer	Dendrimer
Advantages	<ul style="list-style-type: none">* One-pot synthesis* Reduced cost and effort* Similar physical properties to dendrimer* Prepared on a large scale for application	<ul style="list-style-type: none">* Well-defined structure* Monodisperse* Terminal groups located on the surface of a nearly spherical molecule
Disadvantages	<ul style="list-style-type: none">* Low regularity structure with broad molecular weight distribution* Functional groups distributed throughout the molecule	<ul style="list-style-type: none">* Time-consuming and expensive synthesis* Preparation only on a relatively small scale

The field of hyperbranched polymers is certainly no longer new, emerging after an early starting point in the end of 19th century when Berzelius reported the formation of a resin from tartaric acid (A_2B_2 monomer) and glycerol (B_3 monomer).⁶¹ Following the Watson-Smith report of the reaction between phthalic anhydride or phthalic acid and glycerol⁶² in 1901, Callahan, Arsem, Dawson and Howell studied the general reaction, substituting other alcohols and acids for glycerol and phthalic anhydride between 1910 and 1915.^{63,64} In 1909, Baekeland commercially introduced the first hyperbranched phenolic polymers by his Baekeland Company.⁶⁵ In the 1940s, Flory et al. calculated the molecular weight distribution of three-dimensional polymers with trifunctional and tetrafunctional branching units in the state of gelation and introduced the “degree of branching” and “highly branched species” concepts.^{66,67,68,69,70} In 1952, Flory developed the theory that highly branched polymers can be synthesized without the gelation by

polycondensation of a monomer containing one A functional group and two or more B functional ones capable of reacting with A (AB_n monomer),⁷¹ but it was not until 1982 that Kricheldorf obtained highly branched polyesters by copolymerization of AB and AB_2 type monomers.⁷² In 1988, Kim and Webster first generated 'real' hyperbranched polyphenylene polymers by homocoupling of (3,5-dibromophenyl) boronic acid under modified Suzuki conditions, in a mixture of an organic solvent and an aqueous Na_2CO_3 with a catalytic amount of $Pd(PPh_3)_4$.⁷³ Since then, the growth in the field of hyperbranched polymers has been extremely fast, with about 2000 publications in 2004.⁷⁴

Because of their good solubility and excellent processability, three-dimensional hyperbranched conjugated polymers are attracting more and more attention. Hyperbranched polymers can be applied in various fields just like dendrimers,⁷⁵ but hyperbranched polymers are better suited for application than dendrimers because the one-step polymerization process is advantageous when compared with the multi-step synthesis of dendrimers.

Two major pathways have been used for the preparation of hyperbranched polymers. The first one contains techniques of the single-monomer methodology (SMM), in which hyperbranched macromolecules are synthesized by polymerization of AB_n or a latent AB_n monomer (Figure 6.). According to the reaction mechanism, the SMM method includes at least four specific approaches: (1) polycondensation of AB_n monomers;^{76,77} (2) self-condensing vinyl polymerization (SCVP);^{78,79} (3) self-condensing ring-opening polymerization (SCROP);^{80,81} (4) proton-transfer polymerization (PTP).^{82,83} The advantage of

SMM approach to hyperbranched polymers is the lack of gelation. A disadvantage is limited commercial availability of monomers. The other method is double-monomer methodology (DMM) in which direct polymerization of two types of monomers or a monomer pair generates hyperbranched polymers. DMM can be divided into two main subclasses based on the selected monomer pairs and different reaction pathways. The classical ' $A_2 + B_3$ ' method (Figure 7) was first adopted intentionally to prepare soluble hyperbranched polymers by Kakimoto⁸⁴ and Frechet.⁸⁵ Although the $A_2 + B_3$ approach has some merit over SMM approach, such as facile preparation and commercial availability of monomers, it still exhibits the major problem of uncontrollable gelation. To avoid cross-linking, the reaction must be performed under low monomer concentration or slow monomer addition, or the polymerization must be stopped prior to the critical point of gelation. This strongly limits the wide application of the $A_2 + B_3$ approach in large-scale preparation of hyperbranched polymers. Combination of the basic SMM synthetic principle and the ' $A_2 + B_3$ ' methodology generates the couple-monomer methodology (CMM).^{86,87} This new strategy is based on the non-equal reactivity of functional groups in specific monomer pairs. The two monomers would preferentially generate one type of AB_n intermediate *in situ* in the initial stage of polymerization to produce hyperbranched macromolecules without gelation.

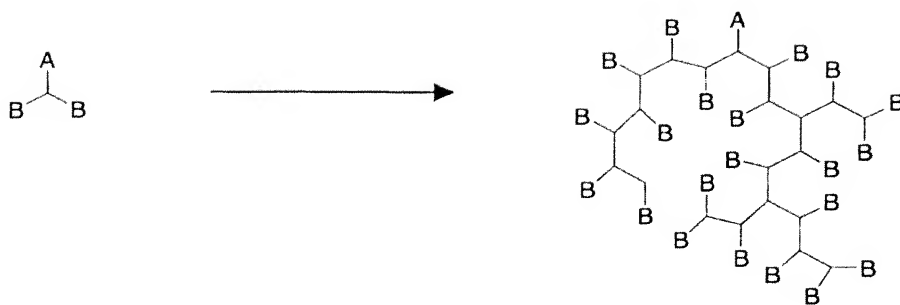


Figure 6. Single-Monomer Methodology (SMM): ---condensation AB_2 .

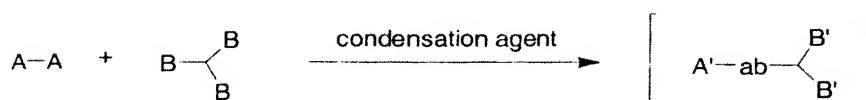


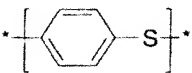
Figure 7. Double-Monomer Methodology (DMM): ---‘ $A_2 + B_3$ ’

Background of polysulfones/polysulfides

Polysulfide and polysulfone polymers have achieved commercial prominence (Table 4). Poly(phenylene sulfide) polymer is used as an engineering plastic for applications requiring good chemical and heat resistance.⁸⁸ However, poly(alkylene sulfide)s are useful elastomers, such as gaskets, gasoline hoses, and sealants.⁸⁹ Their properties can be modified by varying the number of carbon atoms in the repeating unit or the number of sulfur atoms. In recent years attention has centered on aromatic polysulfones due to their good biocompatibility and high permeability of molecular oxygen and carbon dioxide, and excellent hydrolytic stability and the ability to retain mechanical properties in hot, wet

environments.^{90,91,92,93,94,95,96} Overall, sulfide/sulfone polymers are of tremendous industrial significance.

Table 4. Commercially Available Sulfur-Containing Polymers

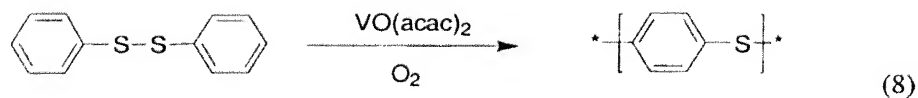
Type	Structure	Typical Uses
Poly(aryl sulfide)		Electronics, electrical, automotive, and machine parts
Poly(alkylene sulfide)	$^{*}+RS_x^{*}$	Sealants, gaskets, hose, solid rocket fuel binder
Polysulfone	$^{*}+ArSO_2^{*}$	Medical and food-processing equipment, piping, Electronics and electrical components, camera cases

A variety of methods have been developed for synthesizing polysulfides.^{97,98,99,100,101,102}

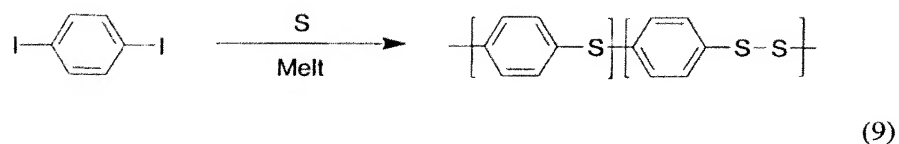
1. Reaction of p-dichlorobenzene with sodium sulfide in a polar solvent at about 250 °C (equation 7).



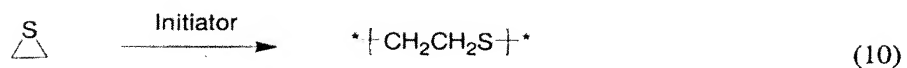
2. Oxidative coupling of diphenyl disulfide with a vanadium catalyst (equation 8)



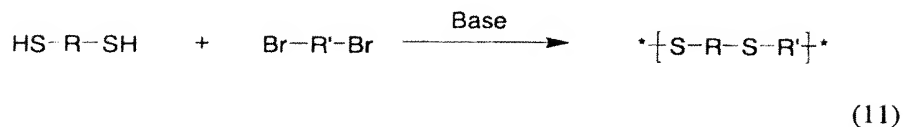
3. Melt condensation of p-iodobenzene with sulfur (equation 9).



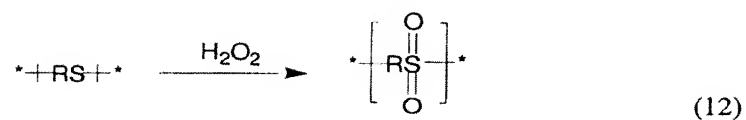
4. Ring-opening polymerization of episulfides (equation 10).



5. Base-catalyzed reaction of dihalides with dithiol (equation 11).

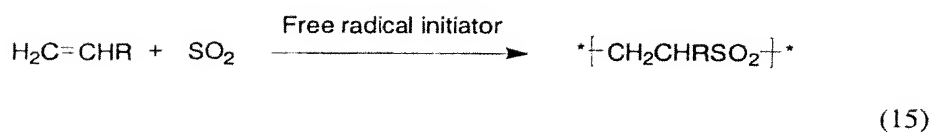
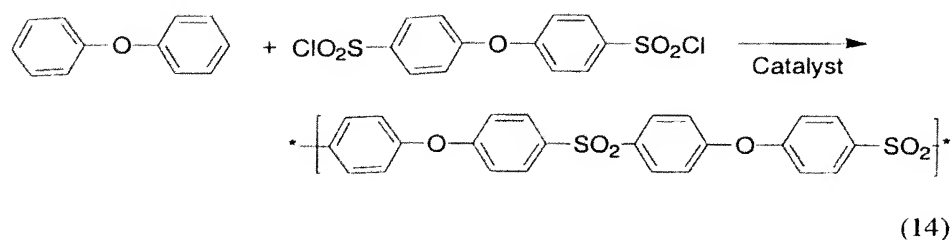
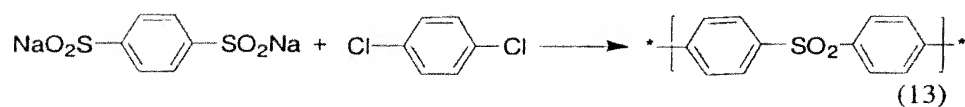


Polysulfones can be prepared from polysulfides by oxidation, for example, with hydrogen peroxide (equation 12).¹⁰³



From the commercial standpoint, however, for aromatic polysulfones the greatest success has been realized with nucleophilic aromatic substitution

(equation 13), Friedel-Crafts-type reaction using sulfonyl chlorides (equation 14) and alternating copolymerization of sulfur dioxide with vinyl monomers (equation 15).^{104,105,106,107}



From the combination of linear aromatic sulfide/sulfone polymers' good biocompatibility and high permeability of molecular oxygen and carbon dioxide, excellent hydrolytic stability and the ability to retain mechanical properties in hot, wet environment with dendritic or hyperbranched polymers' peculiar architecture, we can assume dendritic or hyperbranched aromatic sulfide/sulfone polymers will be attractive materials, but very little work has been done. This work focused on (1) synthesis of arylmethyl sulfone dendrimer using 5-sulfo-isophthalic acid salt as a starting material by convergent method; (2) synthesis and characterization of

hyperbranched poly(phenylene sulfide), poly(phenylene sulfone), core-terminated poly(phenylene sulfide), and end-capped poly(phenylene sulfide).

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Part II

Synthesis and Characterization of Hyperbranched Poly(phenylene Sulfide)/ Poly(phenylene Sulfone)

Introduction

The one-step synthesis allows hyperbranched polymers to be more readily available and prepared on a large scale for potential applications as compared with dendrimers. This attractive feature has led to the development of novel synthetic routes for preparation of hyperbranched polymers, especially the one-step synthesis based on AB_2 monomers which have A and two B functional groups located at 1,3,5 position of a benzene ring. This single-monomer methodology (SMM) was the first method to be developed for hyperbranched polymer synthesis by Kim and Webster in 1988.¹ The hyperbranched polyphenylene was prepared by homocoupling of (3,5-dibromophenyl)boronic acid under modified Suzuki conditions, in a mixture of an organic solvent and an aqueous Na_2CO_3 solution with a catalytic amount of $Pd(PPh_3)_4$ (Scheme 1). In 1991, Frechet reported another one-step synthesis of hyperbranched polyesters by polycondensation reaction of AB_2 monomers method.² The synthesis of the hyperbranched polyester was achieved by thermal self-condensation of 3,5-bis(trimethylsiloxy)benzoyl chloride (Scheme 2) and the average molecular weights was in the range 30 000 to almost 200 000. After that, a broad range of hyperbranched polymers, such as hyperbranched polyethers,^{3,4,5,6} polycarbonates,⁷ polyamides,^{8,9,10} and poly(ether ketone)s^{11,12} are prepared via one-step polycondensation of AB_n monomers. However one-step synthesis of hyperbranched polysulfides / polysulfones is a relatively unexplored field and there are only two literature reports on hyperbranched poly(phenylene sulfide)s

until now. In 1996, Kakimoto¹³ first reported the synthesis of hyperbranched poly(phenylene sulfide) via a poly(sulfonium cation) starting from an AB₂ monomer, methyl 3,5-bis(phenylthio)sulfoxide (Scheme 3). The second report¹⁴ came from our research group, Dr. Hanson's group, where polymerization of commercially available 3,4-dichlorobenzenethiol, unsymmetrical monomer, was accomplished using anhydrous potassium carbonate as a base in the amide solvents N,N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) to give hyperbranched poly(phenylene sulfide) (Scheme 4). Meanwhile, this work was started using 3,5-dichlorobenzenethiol, a symmetrical monomer, to generate the hyperbranched poly(phenylene sulfide) by self-condensation reaction under similar reaction conditions.

The properties of hyperbranched polymers are often affected by the nature of the backbone and the chain end functional groups, degree of branching, chain length, and the molecular weight distribution. Based on the highly branched architecture of hyperbranched polymers, these molecules contain many terminal functional groups which can be modified in order to control the properties of the resulting polymers. Many experiments have been done with the large number of functional end groups attached to the terminal units of hyperbranched polymers. Results showed that the nature of terminal functional groups strongly influenced T_g, solubility and even T_d of hyperbranched polymers.^{15,16} In this work, the numerous chlorine end groups of the hyperbranched poly(phenylene sulfides) were modified by end-capping with naphthalene-1-thiol in order to compare the properties of the polymers. Although peripheral functionalization has received the

most attention, a significant body of research concerns the use of core molecules. Core molecules have been demonstrated to limit molecular weight, reduce polydispersity, and increase the degree of branching within the hyperbranched polymers.^{17,18} In this approach, the growing hyperbranched molecule is coupled with a multifunctional molecule, of B_f type, analogous to the central core of a dendrimer (Scheme 5). The reaction of a core molecule with the single A group of a hyperbranched molecule terminates growth from the focal group.¹⁹ In this work, 1,3,5-trichlorobenzene as core molecule was introduced into the hyperbranched poly(phenylene sulfides).

Characterizing polymers is much more complex than characterizing small molecules and characterizing hyperbranched polymers is even harder than characterizing linear polymers.²⁰ First, molecular weight or molecular weight distribution is an extremely important variable because it relates directly to a polymer's physical properties. Molecular weight values obtained depend in large measure on the method of measurement. Methods that depend on end-group analysis or colligative properties give rise to the number average molecular weight, M_n , because the number of molecules of each weight in the sample is counted. Light scattering and ultracentrifugation, on the other hand, are methods of determining molecular weight based on mass or polarizability of the species present. The greater the mass, the greater is the contribution to the measurement. The value thus obtained is called the weight average molecular weight, M_w . Size exclusion chromatography (SEC) is the most widely used method of determining molecular weight distribution. SEC is a column fractionation method in which

solvated polymer molecules are separated according to their sizes. The technique is also known as gel permeation chromatography (GPC). The separation occurs as the solute molecules in a flowing liquid move through a stationary bed of porous particles. Solute molecules of a given size are sterically excluded from some of the pores of the column packing, which itself has a distribution of pore sizes. Larger solute molecules can permeate a smaller proportion of the pores and thus elute from the column earlier than smaller molecules. Three SEC detectors, differential refractometer, continuous differential viscometer, and light scattering photometer, are widely in use. The difference of the three SEC detectors is in sensitivity. The SEC with differential refractometer, continuous differential viscometer and light scattering photometer was used in this work. Second, spectroscopic methods are commonly employed for studying polymers' structure such as infrared (IR), nuclear magnetic resonance (NMR), and ultraviolet (UV).

Another area of characterization is thermal properties of polymers. One of the most important characteristics of the amorphous state is the behavior of a polymer during its transition from solid to liquid. If an amorphous glass is heated, the kinetic energy of the molecules increases. Motion is still restricted, however, to short-range vibrations and rotations so long as the polymer retains its glasslike structure. As temperature is increased further, there comes a point where the polymer loses its glasslike properties. The temperature at which this takes place is called the glass transition temperature (T_g). If heating is continued, the polymer will eventually lose its elastomeric properties and melt to a flowable liquid. Differential scanning calorimetry (DSC) is a common method for quantitative

studies of thermal transitions in polymers such as temperature of glass transition, T_g ; crystallization, T_c ; crystalline melting point, T_m ; crosslinking; and vaporization. With DSC, a polymer sample and an inert reference are heated in individual heaters, and energy is supplied to keep the sample and reference temperatures constant. In this case, the electrical power difference ($d\Delta Q/dt$) between sample and reference is recorded. Thermal stability is also very important in polymers. When the temperature increases to the point where energy causes bond rupture, the polymer degrades. Thermogravimetric analysis (TGA) is used for determining thermal stability of polymers. The most widely used TGA method is based on continuous measurement of weight on a sensitive balance as sample temperature is increased in air or an inert atmosphere. Data are recorded as a thermogram of weight versus temperature.

Results and discussion

Kinetic Studies for Polymerization. An undergraduate student, James Wilckens, ran a few testing reactions on the 3,4-dichlorobenzenethiolate sodium salt and found this monomer readily polymerized to give an insoluble white polymer under 24 hours at 100 °C condition, with properties similar to those known for linear poly(phenylene sulfide). Shortly thereafter, Alfredo Mellace in our group successfully prepared hyperbranched poly(phenylene sulfide) from 3,4-dichlorobenzenethiol with potassium carbonate in an amide solvent. Polymerization for 24 hours at 100 °C in DMF gave a polymer with a M_w of 17

kD and polydispersity of 2.0. Polymerization for 8.5 hours at 150 °C in NMP gave a polymer with a M_w of 16 kD and polydispersity of 1.5. Based on their results, the monomer, 3,4-dichlorobenzenethiol was switched to 3,5-dichlorobenzenethiol to avoid steric effects and to obtain higher molecular weight. Secondly, only NMP was used as the solvent at higher temperature, 150 °C, to give better polydispersity. Kinetic studies for the polymerization from 3,5-dichlorobenzenethiol with potassium carbonate at 150 °C in NMP was shown in Table 1 and SEC traces of kinetic study of polymerization was observed in Figure 1. The molecular weight of the polymerization increases dramatically from 8 kD to 29 kD when the reaction time is 6 hours and 8 hours respectively. But after 8 hours, the molecular weight of the polymerization decreases sharply, thus the polymer degrades. The molecular weight of the resulting polymer was highly sensitive to the reaction time. The best polymerization time is 8 hours under this condition.

Table 1. M_w as a Function of Polymerization Condition for 3,5-Dichlorobenzenethiol

NMP/150 °C				
Reaction Time (h)	4	6	8	12
M_w	4780	8450	29463	4500

Hyperbranched Poly(phenylene sulfide). Polymerization of commercially available 3,5-dichlorobenzenethiol was accomplished using anhydrous potassium carbonate as a base in NMP at 150 °C for 8 hours to give

hyperbranched poly(phenylene sulfide) (Scheme 6). The crude polymers were isolated by precipitation into aqueous acid (6 M HCl) to quench any remaining thiolate anions. The resulting precipitates were filtered, thoroughly dried under vacuum, and dissolved in a minimal amount of THF at room temperature. The THF solution was then poured into hexanes to precipitate in order to remove low molecular weight constituents and residual NMP. The resulting powdery polymers were isolated by filtration and dried by vacuum again prior to analysis. The polymers were characterized by ^1H NMR (Figure 2), IR (Figure 3), elemental analysis, solubility, size-exclusion chromatography with light-scattering/refractive index detection (SEC-LS/ RI) (Figure 1), differential scanning calorimetry (DSC) (Figure 4), and thermogravimetric analysis (TGA) (Figure 5).

^1H NMR: $\delta=7.11\text{-}7.42$ (m). From ^1H NMR spectrum of the hyperbranched poly(phenylene sulfide), little information can be obtained but it is able to confirm that no small molecules remain. The degree of branching (DB) describes the branching perfection of a hyperbranched polymer in comparison to the respective perfectly branched dendrimer structure.² In the AB_2 system such as 1,3,5-substituted benzene, the degree of branching determined by NMR is usually about 50%-60%.^{21,22} However, for hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol, the degree of branching could not be determined from its ^1H NMR spectrum because the chemical shifts of the aromatic protons are not sufficiently well resolved for this determination.

IR (neat solid): 1547, 1402, 1298, 1100, 843, 793, 667 cm^{-1} .

Elemental Analysis: Anal. Calcd. for hyperbranched poly(phenylene sulfide): C, 50.5; H, 2.1; Cl, 24.8; S, 22.5. Found: C, 50.8; H, 2.17; Cl, 23.6; S, 20.56.

Hyperbranched poly(phenylene sulfide) can be dissolved in THF, DMSO, acetonitrile and NMP but does not dissolve in DMF, dichloromethane, chloroform, hexane, and methanol.

The molecular weight of this hyperbranched poly(phenylene sulfide) was determined by SEC-LS analysis of THF solutions. The light scattering instrument was calibrated against polystyrene standards. Table 2 shows a comparison of hyperbranched poly(phenylene sulfide) from 3,4-dichlorobenzenethiol developed by Alfred Mellace, hyperbranched poly(phenylene sulfide) from poly(sulfonium cation) developed by Jikei, and this hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol. The hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol has the highest molecular weight and the lowest polydispersity compared to hyperbranched poly(phenylene sulfide) from 3,4-dichlorobenzenethiol and hyperbranched poly(phenylene sulfide) from sulfonium cation.

Table 2. Comparison for Three Hyperbranched Poly(phenylene sulfide)s

Starting Material	M_w (kD)	M_w/M_n
Poly(sulfonium cation)	25.7	1.45
3,4-dichlorobenzenethiol	16	1.5
3,5-dichlorobenzenethiol	29	1.1

Poly(phenylene sulfide) (PPS) is notable for its thermal properties. Linear PPS is a semicrystalline polymer with a T_g of 85 °C, a T_m of 285 °C, and a T_c of 225 °C.²³ Thermal behaviors of the hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol were evaluated by differential scanning calorimetry (DSC). The DSC curve of the hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol is given in Figure 4. The hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol was found to be an amorphous polymer with a T_g of 74 °C and a complete lack of crystallinity: no T_m was observed up to 375 °C. Crystallinity could not be induced by annealing (the polymer samples were heated to 300 °C, then slowly cooled back to room temperature). When the annealed samples were reheated to 375 °C, no T_m was observed, although the T_g was observed to be more well-defined. The T_g value of the hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol is similar to those of linear PPS, higher than those of the hyperbranched PPS from 3,4-dichlorobenzenethiol, but lower than those of the hyperbranched PPS from poly(sulfonium cation) shown in Table 3. The similarity between the hyperbranched PPS from 3,4-dichlorobenzenethiol and the hyperbranched PPS from 3,5-dichlorobenzenethiol is that they both are amorphous polymers, no T_c and no T_m observed. However there are no T_c and T_m data obtained by Jikei.

Table 3. Thermal Behaviors of Linear PPS and Hyperbranched PPSs

PPS	T _g (°C)	T _e (°C)	T _m (°C)
Linear PPS	85	225	285
Hyperbranched PPS from 3,5-dichlorobenzenethiol	74	no	no
Hyperbranched PPS from 3,4-dichlorobenzenethiol	60	no	no
Hyperbranched PPS from poly(sulfonium cation)	124	na	na

Thermogravimetric analysis shows that linear PPS is quite thermally stable. Under a N₂ atmosphere, linear PPS was determined to have an onset temperature for decomposition (T_d) of 480 °C, a maximum decomposition (T_{max}) of 520 °C and more than 50% of the polymer remains as a residue at 700 °C. Under an air atmosphere, linear PPS was found to have two decomposition events: a first T_d of 480 °C with a T_{max} of 510 °C, and a second T_d' of 565 °C with a T_{max}' of 575 °C. The 700 °C residue is less than 5%. TGA revealed that the hyperbranched PPS from 3,5-dichlorobenzenethiol was more stable than the hyperbranched PPS from 3,4-dichlorobenzenethiol, although not as stable as linear PPS. Table 4 lists the values for linear PPS, the hyperbranched PPS from 3,4-dichlorobenzenethiol and the hyperbranched PPS from 3,5-dichlorobenzenethiol under both N₂ and air atmosphere. Under N₂ atmosphere, the hyperbranched PPS from 3,5-dichlorobenzenethiol has an onset temperature for decomposition of 450 °C, a maximum decomposition of 480 °C, and 48% of the polymer remains as a residue

at 700 °C. Under an air atmosphere, the hyperbranched PPS from 3,5-dichlorobenzethiol has two decomposition events: a first T_d of 410 °C with a T_{max} of 450 °C and a second T_d' of 560 °C with a T_{max}' of 600 °C. The 700 °C residue is less than 3%. Figure 5 shows typical TGA curves for the hyperbranched PPS from 3,5-dichlorobenzethiol.

Table 4. Thermogravimetric Analysis of PPSs

Sample (atmosphere)	T_d (°C)	T_{max} (°C)	T_d' (°C)	T_{max}' (°C)	residue (%)
Linear PPS(N ₂)	480	520			
Hyperbranched PPS from 3,4-dichlorobenzenethiol(N ₂)	442	472			
Hyperbranched PPS from 3,5-dichlorobenzenethiol(N ₂)	450	480			
Linear PPS(air)	480	510	565	575	<5%
Hyperbranched PPS from 3,4-dichlorobenzenethiol(air)	418	452	550	559	2%
Hyperbranched PPS from 3,5-dichlorobenzenethiol(air)	410	450	560	600	3%

Hyperbranched Poly(phenylene sulfone). Oxidation of the hyperbranched poly(phenylene sulfide) to hyperbranched poly(phenylene sulfone) was readily accomplished with hydrogen peroxide in acetic acid (Scheme 7). The resulting sulfone polymer is insoluble in all common solvents including THF, DMF, DMSO, and NMP. Its structure was confirmed by IR (Figure 6) and elemental analysis. Two characteristic IR-absorption bands of the sulfone polymer with SO₂ groups were observed at 1340 and 1160 cm⁻¹. Table 5 lists elemental analysis and

expected data for the sulfone polymer. It is difficult to determine O directly, but determination of C, H, S, and Cl accounted for 89.90% of the mass, leaving 10.10% unaccounted for and assigned to O. The expected percentage of O for a hyperbranched poly(phenylene sulfone) is 18.26%. The result of elemental analysis shows that the oxidation to the sulfone is not complete, about 54% conversion.

Table 5. Elemental Analysis of Hyperbranched Poly(phenylene sulfone)

	C (%)	H (%)	Cl (%)	S (%)	O (%)
Calculated	41.14	1.74	20.55	18.31	18.26
Found	43.5	1.94	26.74	18.17	10.1

DSC analysis of the hyperbranched sulfone polymer revealed a T_g of 203 °C, which is similar to linear aromatic polysulfones with T_g of > 200 °C and higher than the hyperbranched sulfone polymer from 3,4-dichlorobenzenethiol with a T_g of 155 °C observed by Alfredo Mellace. There was no detectable T_m . The hyperbranched PPSO₂ had a much higher T_g than its original hyperbranched PPS. TGA analysis revealed that the decomposition of the PPSO₂ polymer began at a lower temperature than PPS but the maximum decomposition of the PPSO₂ polymer is at a higher temperature than PPS (Table 6). Under N₂ atmosphere, the hyperbranched PPSO₂ has an onset temperature for decomposition of 420 °C, a maximum decomposition of 510 °C, and 41% of the polymer remains as a residue at 700 °C. Under an air atmosphere, the hyperbranched PPSO₂ has a T_d of 420 °C with a T_{max} of 510 °C. The 700 °C residue is 0%. The thermal stability of the

hyperbranched PPSO₂ is better than the thermal stability of the hyperbranched PPS. DSC and TGA curves of the hyperbranched poly(phenylene sulfone) are shown in Figures 7 and 8.

Table 6. DSC/TGA Data for Hyperbranched Poly(phenylene sulfone)

Sample (atmosphere)	T _g (°C)	T _d (°C)	T _{max} (°C)	T _d ' (°C)	T _{max} ' (°C)	residue (%)
Hyperbranched PPS(N ₂)		450	480			
Hyperbranched PPSO ₂ (N ₂)		420	510			
Hyperbranched PPS (air)	74 (annealed)	410	450	550	600	3%
Hyperbranched PPSO ₂ (air)	203 (annealed)	420	510			0%

Introduction of a Phenylene Core to the Focal Point of the Hyperbranched Poly(phenylene sulfide). Polymerization of AB₂ monomers in the presence of a B₃ core is known to reduce the polydispersity of the resulting hyperbranched polymers while also reducing the molecular weight.²⁴ 1,3,5-trichlorobenzene was used as a trifunctional core for preparation of hyperbranched PPS under these condition (Scheme 8). Polymerization employing this core was accomplished in NMP as solvent with a ratio of 1 core molecule per 50 monomers (1:50) conditions. The reaction with the 1,3,5-trichlorobenzene core was conducted using procedure identical to that described above for the polymer without core including time and temperature of reaction, method of isolation, and purification conditions. The hyperbranched poly(phenylene sulfide) with the 1,3,5-trichlorobenzene core was characterized by elemental analysis, size-

exclusion chromatography with light-scattering detection (SEC-LS), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA).

The proposed structure was supported by elemental analysis, calculated: C, 50.50; H, 2.1; Cl, 24.8; S, 22.5. and found: C, 50.25; H, 1.90; Cl, 25.46; S, 22.39.

The SEC-LS data for the hyperbranched poly(phenylene sulfide) with the 1,3,5-trichlorobenzene core and the hyperbranched poly(phenylene sulfide) without core are summarized in Table 7. As expected for hyperbranched polymers, addition of a core forming B₃ molecule results in lower M_w and low M_w/M_n values observed by Alfredo Mellace, but the hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol with the 1,3,5-trichlorobenzene core has a significant lower M_w than the hyperbranched poly(phenylene sulfide) from 3,5-dichlorobenzenethiol without core and retains the same M_w/M_n value. Because M_w/M_n value for the hyperbranched PPS without core is 1.1, there is little room to be improved for the hyperbranched PPS with the core.

Table 7. SEC-LS Data for Hyperbranched PPS with and without Core

Hyperbranched PPS	M_w (kD)	M_w/M_n
No core	29	1.1
Core	14	1.1

DSC analysis of the hyperbranched PPS with the core polymer revealed a T_g of 66 °C, which is slightly lower than the hyperbranched PPS, but no

detectable T_m . TGA analysis revealed that the decomposition of the hyperbranched PPS with the core polymer began at a high temperature in N_2 atmosphere and in air atmosphere (Table 8). Under N_2 atmosphere, the hyperbranched PPS with the core has an onset temperature for decomposition of 475 °C, a maximum decomposition of 480 °C, and 40% of the polymer remains as a residue at 700 °C. Under an air atmosphere, the hyperbranched PPS with the core has a T_d of 420 °C with a T_{max} of 545 °C. The 700 °C residue is 8%. The thermal stability of the hyperbranched PPS with the core is better than the hyperbranched PPS but its T_g is slightly lower. DSC and TGA curves of the hyperbranched PPS with the core are shown in Figures 9 and 10.

Table 8. DSC/TGA Data for Hyperbranched PPS with and without Core

Hyperbranched PPS (atmosphere)	T_g (°C)	T_d (°C)	T_{max} (°C)	T_d' (°C)	T_{max}' (°C)	residue (%)
No core(N_2)		450	480			
Core (N_2)		475	480			
No core PPS (air)	74 (annealed)	410	450	550	600	3%
Core (air)	66 (annealed)	420	545			8%

Introduction of Naphthalene Units to the Chain Ends Group of the Hyperbranched Poly(phenylene sulfide). It is known that the nature of the terminal groups has a major impact on the thermal properties of dendritic and hyperbranched polymers. Naphthalene thiol was used to replace chlorine on the end of the hyperbranched PPS for preparation of the hyperbranched end-capped

PPS under these condition (Scheme 9). Polymerization employing naphthalene units was accomplished in NMP as solvent and a ratio of 1 end-capped molecule per monomer (1:1). The reaction with the naphthalene as an end unit was conducted using a similar procedure to that described above for the hyperbranched PPS including time and temperature of reaction, method of isolation, and purification conditions except adding naphthalene thiol into the reaction mixture six hours later. The hyperbranched end-capped poly(phenylene sulfide) with naphthalene was characterized by UV, elemental analysis, size-exclusion chromatography with light-scattering detection (SEC-LS), solubility, differential scanning calorimetry (DSC), and thermalgravimetric analysis (TGA).

From UV spectrum (Figures 11, 12), a difference between the hyperbranched end-capped PPS and the hyperbranched PPS is that the hyperbranched end-capped PPS has a significant absorption at 220 nm but the hyperbranched PPS does not absorb at 220 nm.

Elemental analysis shows that the chlorine for the hyperbranched end-capped PPS drops from 24.8% to 8.01%. It suggests that about 2/3 (67%) of the chlorine was replaced by naphthalenes.

The SEC-LS data for the hyperbranched poly(phenylene sulfide) with the end-capped naphthalenes and the comparison with the hyperbranched poly(phenylene sulfide) without end-capped are summarized in Table 9. The hyperbranched PPS with the end-capped naphthalenes has lower M_w and higher M_w/M_n values.

Table 9. SEC-LS Data for Hyperbranched PPS with and without End-caps

Hyperbranched PPS	M_w (kD)	M_w/M_n
No end-caps	29	1.1
End-caps	18	1.2

The end-capped hyperbranched PPS polymers increase their solubility in organic solvents in comparison with the hyperbranched PPS polymers. For example, the end-capped hyperbranched PPS polymers can be easily dissolved in methylene chloride and chloroform.

DSC analysis of the hyperbranched PPS with the core polymer revealed a T_g of 74.5 °C, which is slightly higher than the hyperbranched PPS. There was no detectable T_m . This result shows that the replacement of aromatic chlorines on the end of the hyperbranched PPS can increase T_g value. It is consistent with those results observed by Girolamo and Frechet.^{25,26} TGA analysis revealed that the decomposition of the hyperbranched PPS with the end-capped polymer began at a low temperature in N₂ atmosphere and in air atmosphere (Table 10). Under N₂ atmosphere, the hyperbranched PPS with the core has an onset temperature for decomposition of 420 °C, a maximum decomposition of 495 °C, and 50% of the polymer remains as a residue at 700 °C. Under an air atmosphere, the hyperbranched PPS with the end-capped has a T_d of 375 °C with a T_{max} of 480 °C. The 700 °C residue is 2%. The thermal stability of the hyperbranched PPS with

the end-caps is worse than the hyperbranched PPS in N₂ atmosphere and in air atmosphere, but its T_g is slightly higher. DSC and TGA curves of the hyperbranched PPS with the end-capped are shown in Figures 13 and 14.

Table 10. DSC/TGA Data for the Hyperbranched PPS with and without End-caps

Hyperbranched PPS (atmosphere)	T _g (°C)	T _d (°C)	T _{max} (°C)	T _d ' (°C)	T _{max} ' (°C)	residue (%)
No end-caps (N ₂)		450	480			
End-caps (N ₂)		420	495			
No end-caps (air)	74.0 (annealed)	410	450	550	600	3%
End-caps (air)	74.5 (annealed)	375	480			2%

Conclusion

Hyperbranched poly(phenylene sulfide) can be readily prepared from 3,5-dichlorobenzenethiol by heating polymerization. The resulting polymers have a high M_w (29 kD) and a narrow polydispersity, and show excellent thermal stability, but are essentially noncrystalline and significantly more soluble. Addition of a trivalent core reduced the M_w , but the resulting polymers had better thermal stability than those of the polymers without core. End-capped hyperbranched poly(phenylene sulfide) had a lower M_w (18 kD) and a slightly wide polydispersity, but the resulting polymers had worse thermal properties than those of the polymers without end-capped. Oxidation of hyperbranched PPS

provides insoluble hyperbranched poly(phenylene sulfone), but the resulting polymers had a high glass transition temperature.

Experimental

General. Except as noted, all materials were purchased from commercial suppliers and used without further purification. Linear poly(phenylene sulfide) resin was purchased from Monomer-Polymer and Dajac Laboratories, Feasterville, PA. Potassium carbonate was dried 24 hours in an oven at 200 °C before use. Reactions were run in three-necked round-bottom flasks with condenser, efficient magnetic stirrer, and N₂ line. All reaction vessels were dried with a heat gun under vacuum and then flushed with N₂ for 15 minutes. Reaction temperatures were maintained by a Thermo-watch LS1000. IR spectra were recorded on the neat solids using a Perkin-Elmer Spectrum One FT-IR spectrophotometer at 4 cm⁻¹ resolution. Nuclear magnetic resonance spectra were obtained on a Varian 300 MHz FT-NMR spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Calculated elemental analyses were based on the degree of polymerization of the given polymer sample. UV spectra were obtained on a Beckman Coulter DC-70 UV/Vis spectrophotometer.

Size-Exclusion Chromatography. The SEC LS/RI system was composed of a Waters 510 Pump with an online degasser, a refractometer and a Precision

Detectors 2000 light scattering unit with 15° and 90° detectors. The stationary phase was a cross-linked polystyrene column from Polymer Laboratories (5- μ m particle size, 500-A pore size) with a guard column. Chromatograms were run using inhibitor-free THF at a flow rate of 1.0 mL/min and an injection volume of 50 μ l with a sample concentration of 2.0 mg/mL. Column temperature was maintained at 30 $^{\circ}$ C for all sample runs. All samples were filtered using a 0.45 μ m filter into pre-rinsed vials using inhibitor-free THF before injection.

Differential Scanning Calorimetry. DSC data were obtained on a TA Instrument 2920 calorimeter with a high-resolution sample chamber. Samples were placed in hermetically sealed aluminum pans and weighted on a microbalance. Best results were obtained by annealing the samples at 200 $^{\circ}$ C or 300 $^{\circ}$ C for 60 minutes prior to analysis. Analysis was performed by raising the temperature from 0 to 375 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min. Glass transition temperatures were identified from midpoints using TA Universal Analysis software.

Thermogravimetric Analysis. TGA data were obtained on a TA Instruments HiRes TGA 2950 thermogravimetric analyzer. Samples were placed in platinum pans and heated from 30 to 700 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min. Onset temperature (T_d) and maximum decomposition temperature (T_{max}) were identified using TA Universal Analysis software.

Poly(phenylene sulfide) (PPS). General Procedure: 3,5-dichlorobenzenethiol (1 g, 5.58 mmole) was added to potassium carbonate (4.63 g, 33.5 mmole) in 10 mL of 1-methyl-2-pyrrolidinone (NMP). The reaction mixture was purged with N_2 or Argon a few times and heated to 150 $^{\circ}$ C in an oil

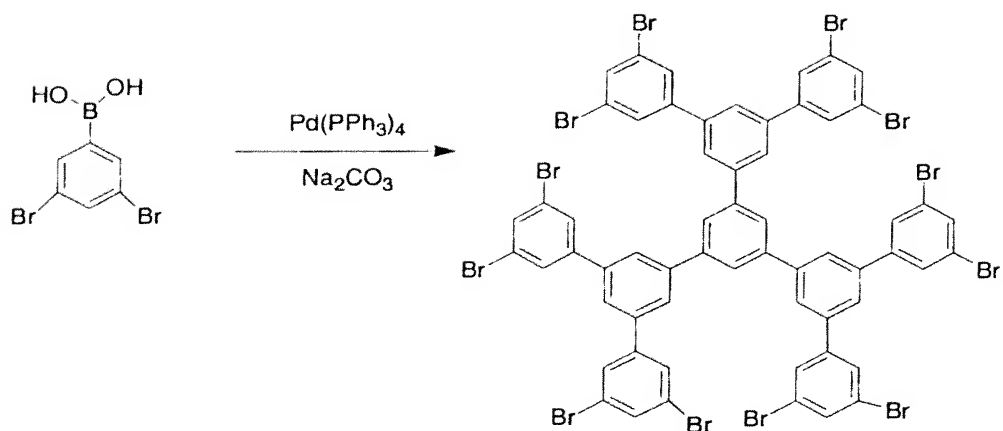
bath for 8 hours. After cooling to room temperature, ice-water and 6 N HCl were added to quench the reaction. The resulting precipitate was vigorously stirred for 1 hour and then filtered. The precipitate was dried thoroughly under vacuum and then dissolved with vigorous stirring in a minimal amount of THF. The THF solution was added dropwise to hexanes with vigorous stirring over 2 hours. This precipitate was then filtered, washed with hexanes and dried under vacuum. The final quantity of the precipitated polymer obtained after workup was about 0.8 g as a pale tan powder.

Poly(phenylene sulfone) (PPSO₂). 250 mg of poly(phenylene sulfide) was added to 12mL of 30% hydrogen peroxide and 20mL of acetic acid. The resulting suspension was refluxed for 4 hours, cooled, and precipitated slowly by pouring into a well-stirred solution of saturated sodium bicarbonate. The resulting precipitate was then filtered, washed with water, and dried. The hyperbranched poly(phenylene sulfone) polymer obtained was finely divided white powder. The quantity obtained was 185 mg (60% yield, based on full oxidation).

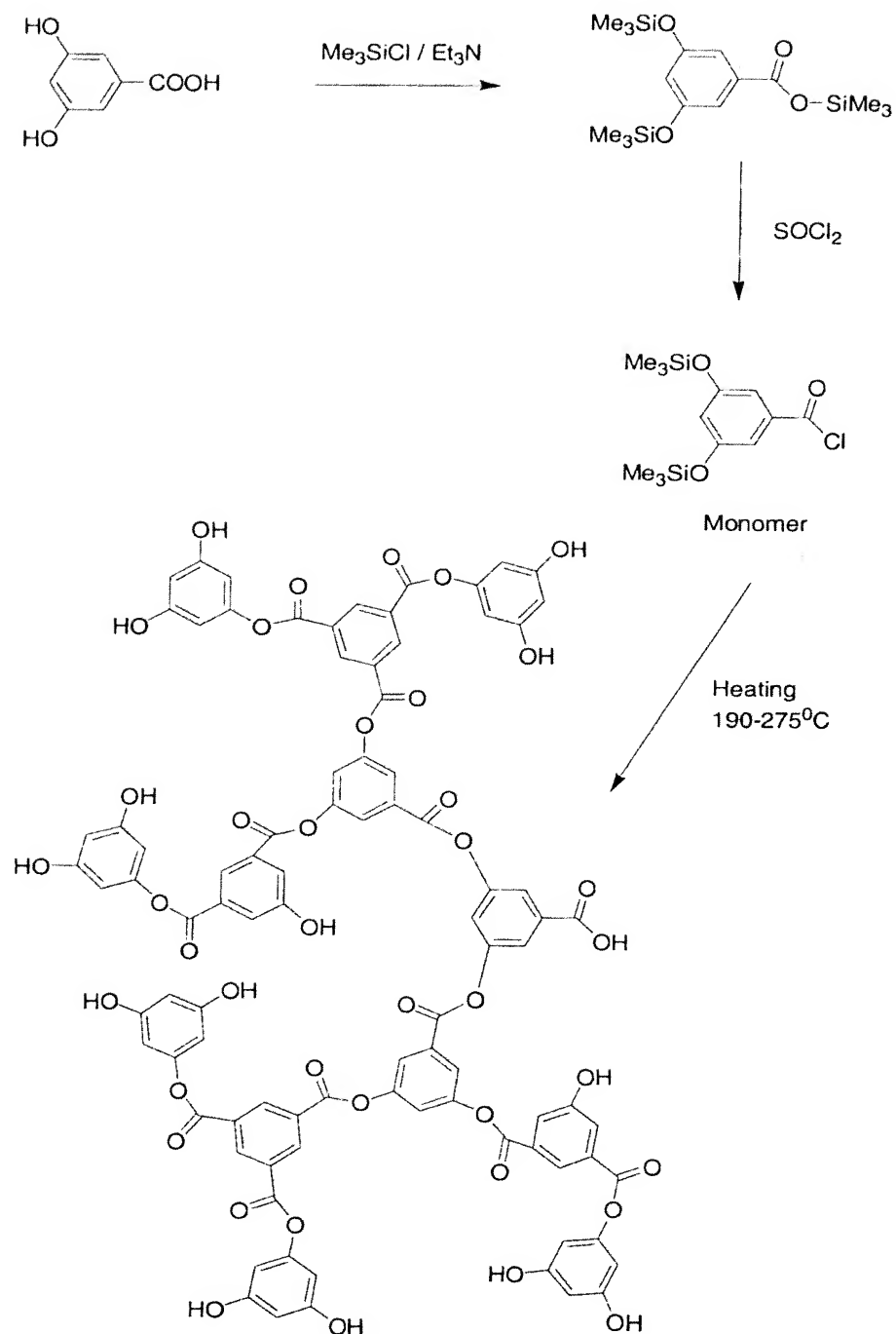
Poly(phenylene sulfide) with core (PPS with core). 3,5-dichlorobenzenethiol (1 g, 5.58 mmole) was added to 1,3,5-trichlorobenzene (0.02 g, 0.11 mmole) and potassium carbonate (4.63 g, 33.5 mmole) in 15mL of 1-methyl-2-pyrrolidinone (NMP). The reaction mixture was purged with N₂ or Ar a few times and heated to 150 °C in an oil bath for 8 hours. After cooling to room temperature, ice-water and 6 N HCl were added to quench the reaction. The workup was the same as the general procedure above. The polymer had the same

appearance with a core a tan powder. The final quantity of polymer sample obtained was 0.8 g.

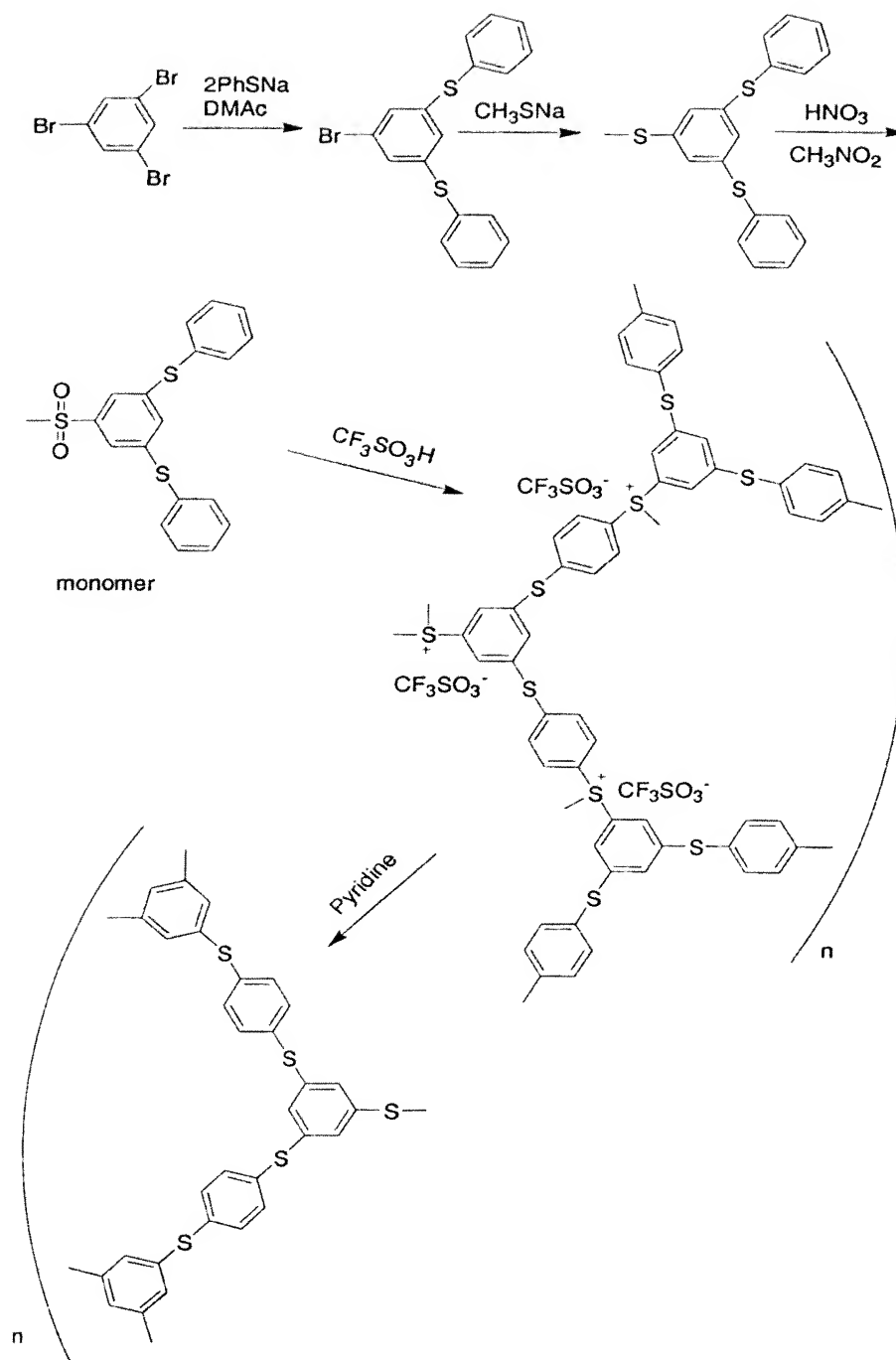
End-capped Poly(phenylene sulfide) (PPS with end-caps). 3,5-dichlorobenzenethiol (1 g, 5.58 mmole) was added to potassium carbonate (4.63 g, 33.5 mmole) in 10mL of 1-methyl-2-pyrrolidinone (NMP). The reaction mixture was purged with N₂ or Ar a few times and heated to 150 °C in an oil bath for 6 hours. 1-Naphthalene thiol (0.89 g 33.5 mmole) was added to the reaction mixture in one portion and the reaction maintained at 150 °C for another two hours. After cooling to room temperature, ice-water and 6 N HCl were added to quench the reaction. The workup was the same as the general procedure above. The polymer had the same appearance with end-caps as without end-caps. The final quantity of polymer sample obtained was 0.75 g.



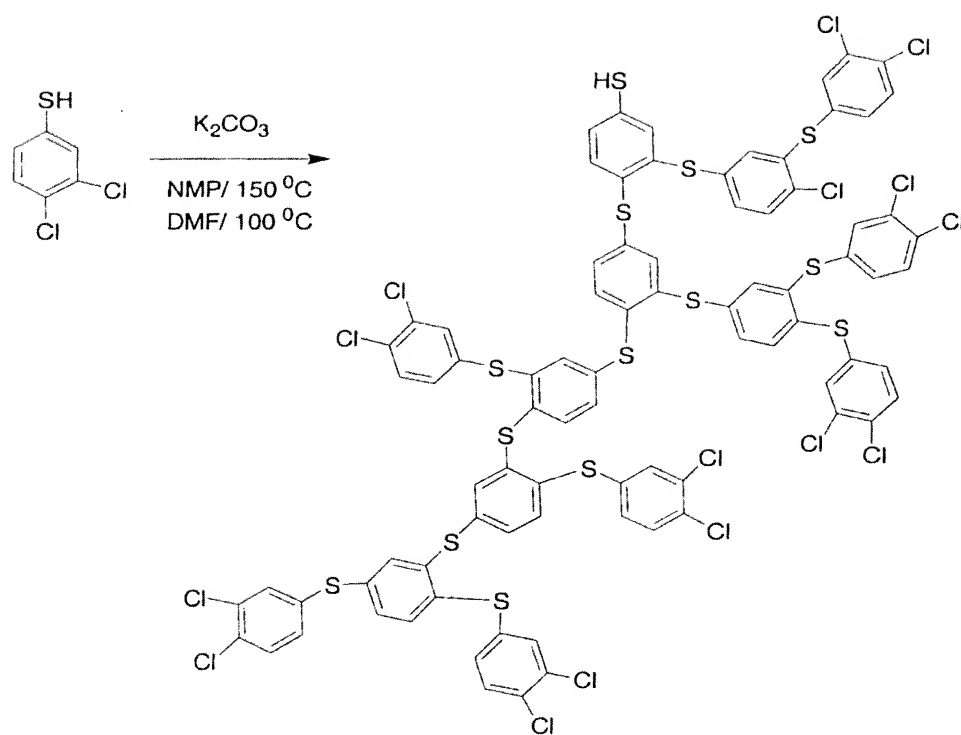
Scheme 1. Synthesis of hyperbranched polyphenylene via polycondensation reaction of AB_n monomers by Kim and Webster in 1988 (ref. 1).



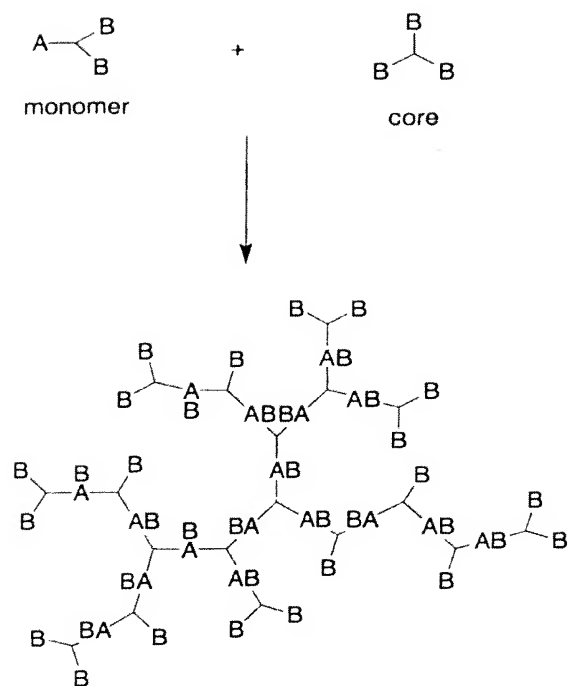
Scheme 2. Synthesis of hyperbranched polyesters via polycondensation reaction of AB_n monomers by Frechet in 1991 (ref. 2).



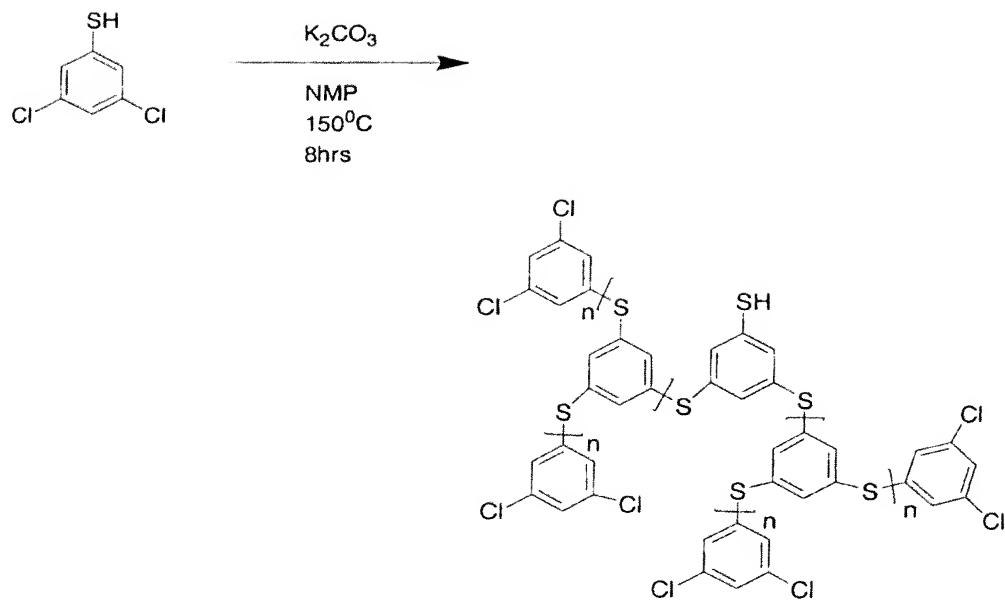
Scheme 3. Synthesis of hyperbranched polysulfides via polycondensation reaction of AB_n monomers by Kakimoto in 1996 (ref. 13).



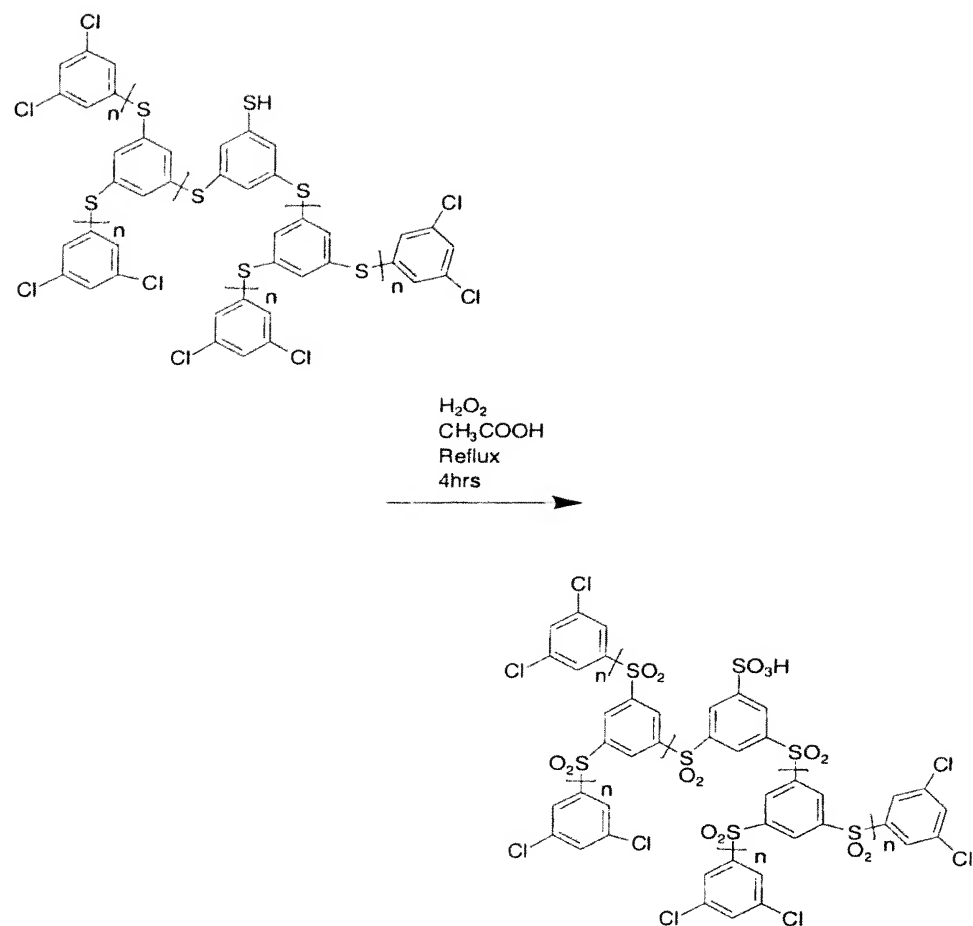
Scheme 4. Synthesis of hyperbranched polysulfides via polycondensation reaction of AB_n monomers by Hanson's group in 2005 (ref. 14).



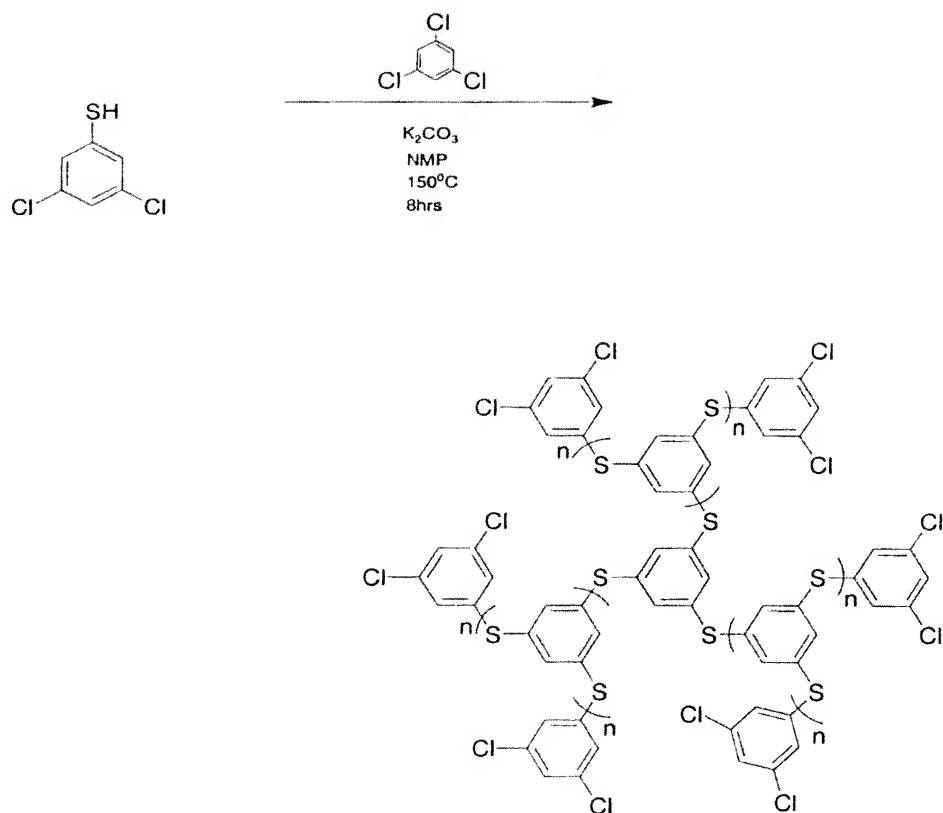
Scheme 5. An idealized AB₂/B₃ core-terminated hyperbranched polymer (ref. 19).



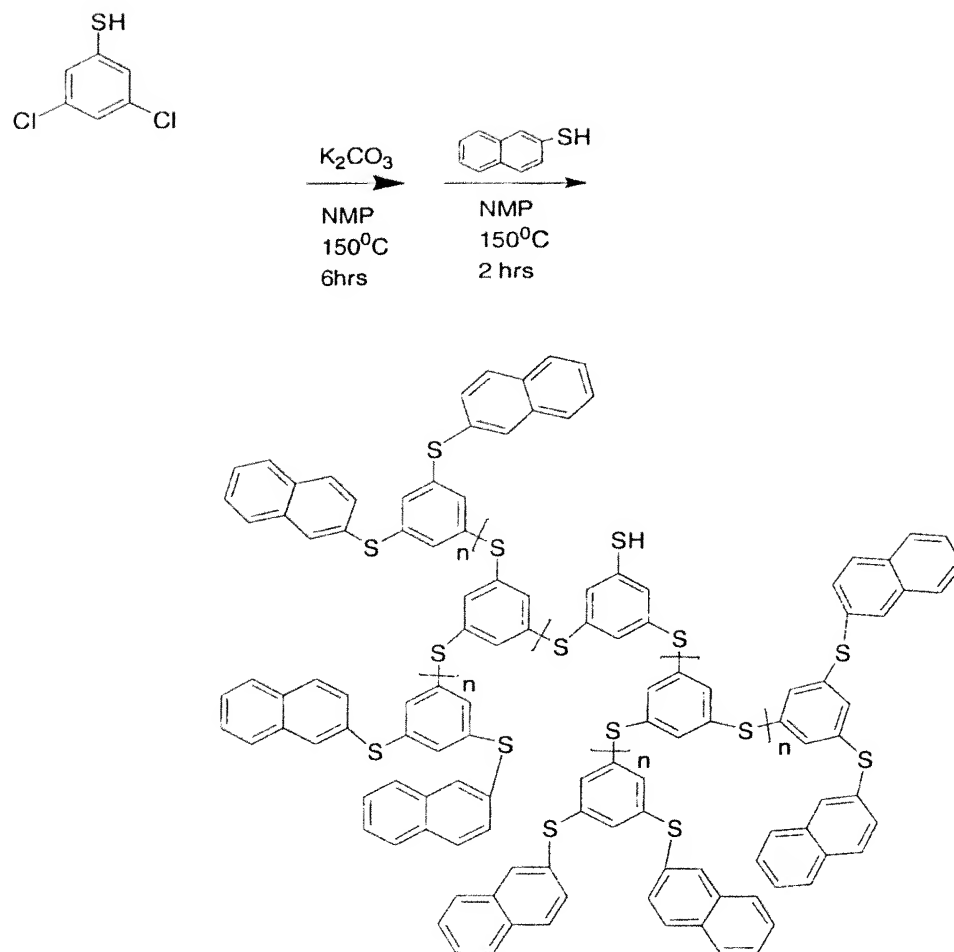
Scheme 6. Polymerization of 3,5-dichlorobenzenethiol to a hyperbranched poly(phenylene sulfide)



Scheme 7. Synthesis of hyperbranched poly(phenylene sulfone) via a hyperbranched poly(phenylene sulfide).



Scheme 8. Polymerization of 3,5-dichlorobenzenethiol with 1,3,5-trichlorobenzene as a multifunctional core.



Scheme 9. Polymerization of 3,5-dichlorobenzenethiol with Naphthalene as end-capped units.

Table 1. M_w as a Function of Polymerization Condition for 3,5-Dichlorobenzenethiol

NMP/150 °C				
Reaction Time (h)	4	6	8	12
M_w	4780	8450	29463	4500

Table 2. Comparison for Three Hyperbranched Poly(phenylene sulfide)s

Starting Material	M_w (kD)	M_w/M_n
Sulfonium cation	25.7	1.45
3,4-dichlorobenzenethiol	16	1.5
3,5-dichlorobenzenethiol	29	1.1

Table 3. Thermal Behaviors of Linear PPS and Hyperbranched PPSs

PPS	T_g (°C)	T_c (°C)	T_m (°C)
Linear PPS	85	225	285
Hyperbranched PPS from 3,5-dichlorobenzenethiol	74	no	no
Hyperbranched PPS from 3,4-dichlorobenzenethiol	60	no	no
Hyperbranched PPS from sulfonium cation	124	na	na

Table 4. Thermogravimetric Analysis of PPSs

Sample (atmosphere)	T _d (°C)	T _{max} (°C)	T _d ' (°C)	T _{max} ' (°C)	residue (%)
Linear PPS(N ₂)	480	520			
Hyperbranched PPS from 3,4-dichlorobenzenethiol(N ₂)	442	472			
Hyperbranched PPS from 3,5-dichlorobenzenethiol(N ₂)	450	480			
Linear PPS(air)	480	510	565	575	<5%
Hyperbranched PPS from 3,4-dichlorobenzenethiol(air)	418	452	550	559	2%
Hyperbranched PPS from 3,5-dichlorobenzenethiol(air)	410	450	560	600	3%

Table 5. Elemental Analysis of Hyperbranched Poly(phenylene sulfone)

	C (%)	H (%)	Cl (%)	S (%)	O (%)
Calculated	41.14	1.74	20.55	18.31	18.26
Found	43.5	1.94	26.74	18.17	10.1

Table 6. DSC/TGA Data for Hyperbranched Poly(phenylene sulfone)

Sample (atmosphere)	T _g (°C)	T _d (°C)	T _{max} (°C)	T _d ' (°C)	T _{max} ' (°C)	residue (%)
Hyperbranched PPS(N ₂)		440	480			
Hyperbranched PPSO ₂ (N ₂)		420	510			
Hyperbranched PPS (air)	74 (annealed)	410	450	550	600	3%
Hyperbranched PPSO ₂ (air)	203 (annealed)	420	510			0%

Table 7. SEC-LS Data for Hyperbranched PPS with and without Core

Hyperbranched PPS	M _w (kD)	M _w /M _n
No core	29	1.1
Core	14	1.1

Table 8. DSC/TGA Data for Hyperbranched PPS with and without Core

Hyperbranched PPS (atmosphere)	T _g (°C)	T _d (°C)	T _{max} (°C)	T _d ' (°C)	T _{max} ' (°C)	residue (%)
No core(N ₂)		450	480			
Core (N ₂)		475	480			
No core PPS (air)	78 (annealed)	410	450	550	600	3%
Core (air)	66 (annealed)	420	545			8%

Table 9. SEC-LS Data for Hyperbranched PPS with and without End-caps

Hyperbranched PPS	M_w (kD)	M_w/M_n
No end-caps	29	1.1
End-caps	18	1.2

Table 10. DSC/TGA Data for Hyperbranched PPS with and without End-caps

Hyperbranched PPS (atmosphere)	T_g (°C)	T_d (°C)	T_{max} (°C)	T_d' (°C)	T_{max}' (°C)	residue (%)
No end-caps(N ₂)		450	480			
End-caps (N ₂)		420	495			
No end-caps (air)	74.0 (annealed)	410	450	550	600	3%
End-cap (air)	74.5 (annealed)	375	480			2%

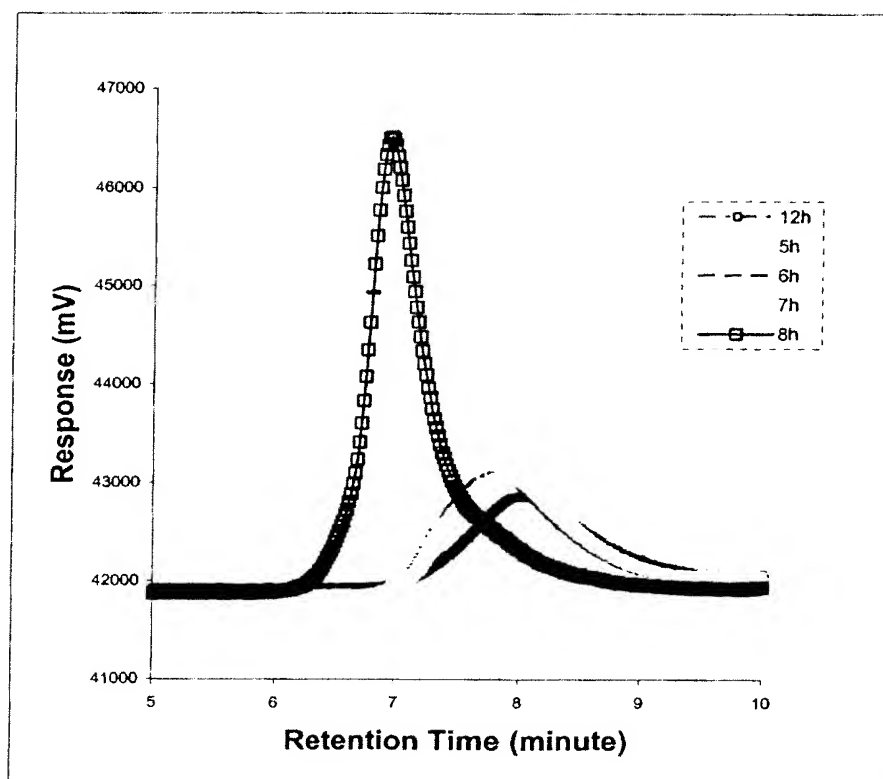


Figure 1. SEC traces of kinetic study of polymerization under NMP as a solvent and 150 °C condition.

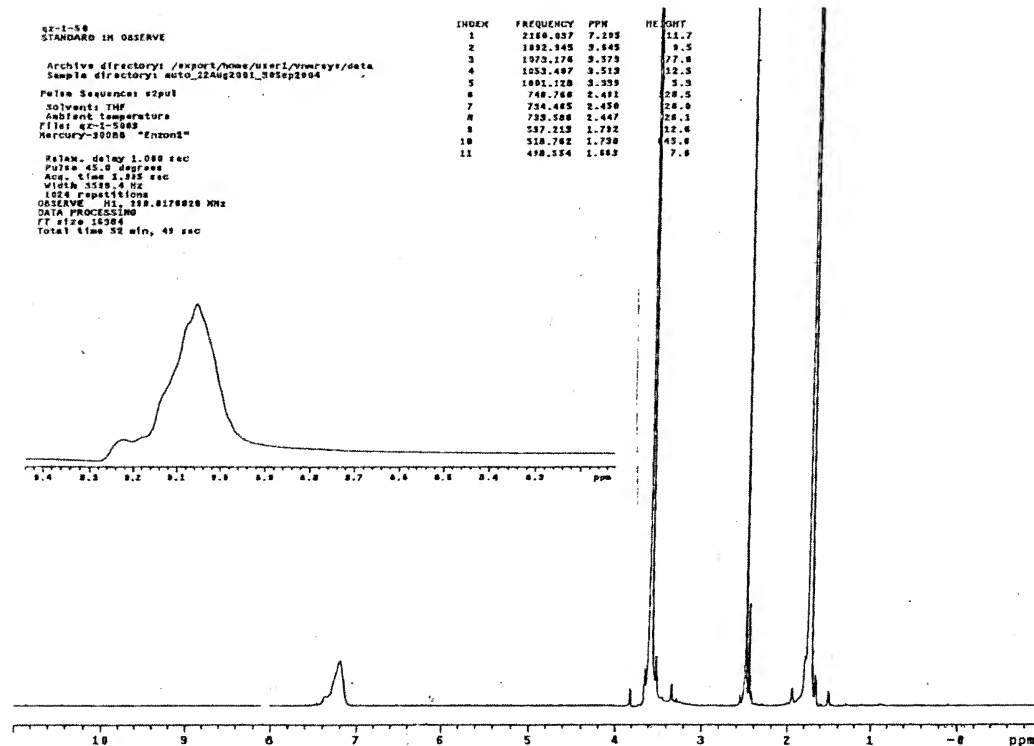


Figure 2. ^1H NMR spectrum of hyperbranched poly(phenylene sulfide).

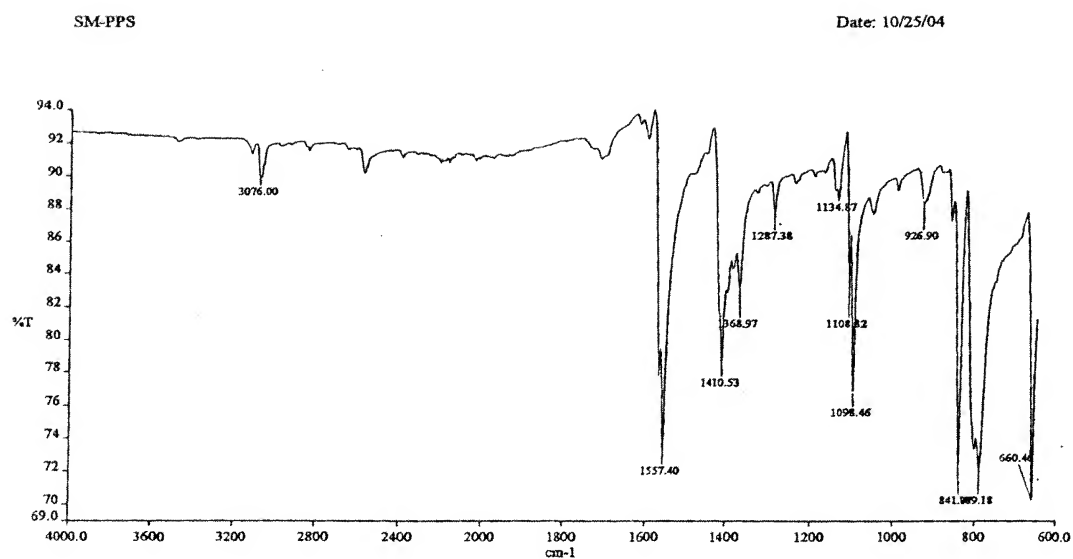


Figure 3. IR spectrum of hyperbranched poly(phenylene sulfide).

Sample: polysulfide without core
Size: 1.8210 mg
Method: pps mixing
Comment: polysulfide without core

DSC

File: C:\...lucy\polysulfide without core.001
Operator: Lucy Zhao
Run Date: 14-Jun-04 15:27

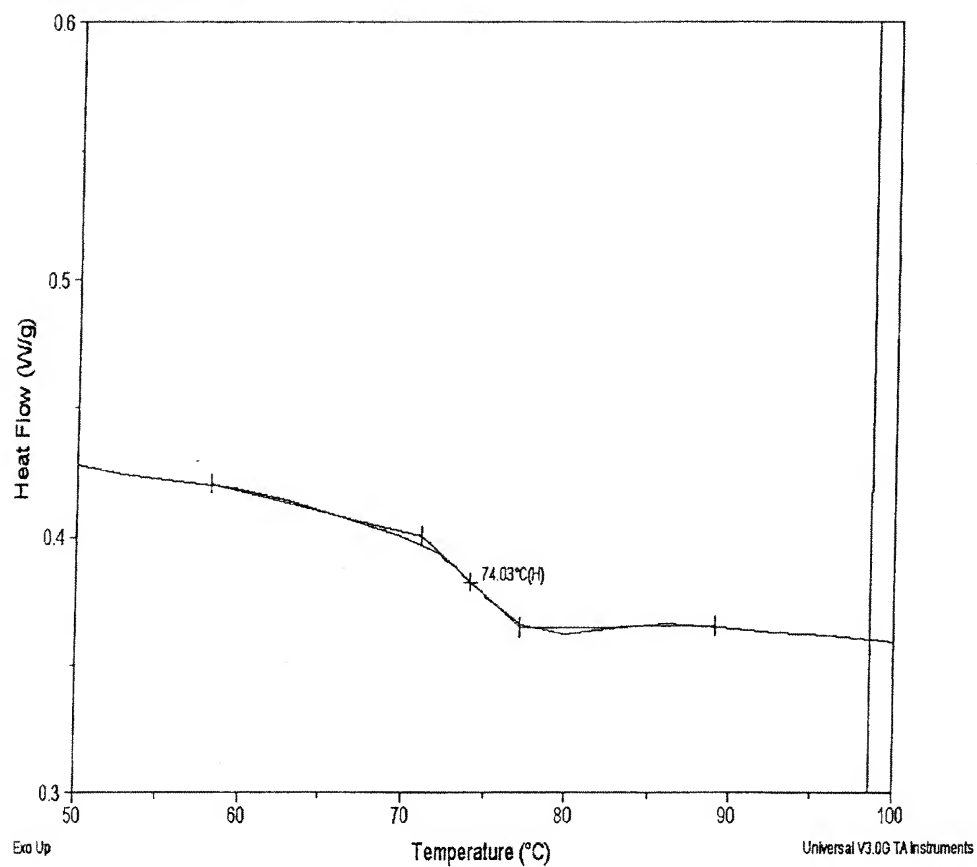


Figure 4. DSC of hyperbranched poly(phenylene sulfide).

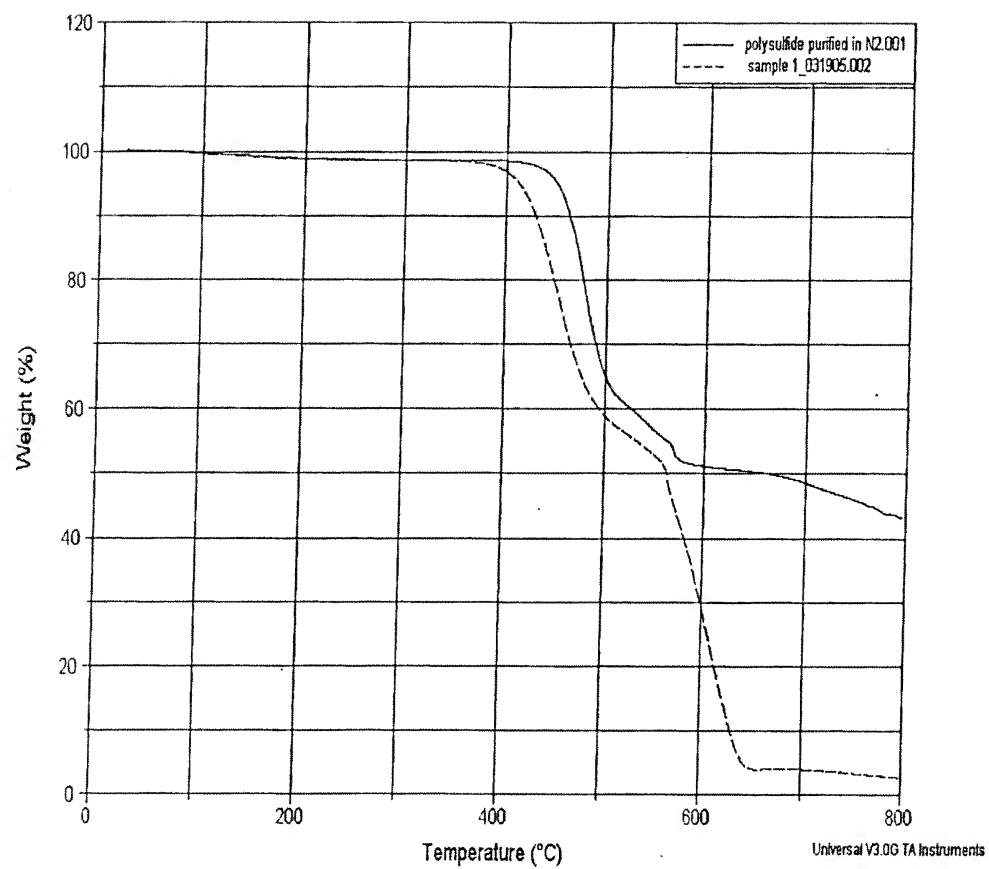


Figure 5. TGA of hyperbranched poly(phenylene sulfide) under N₂ and air atmosphere.

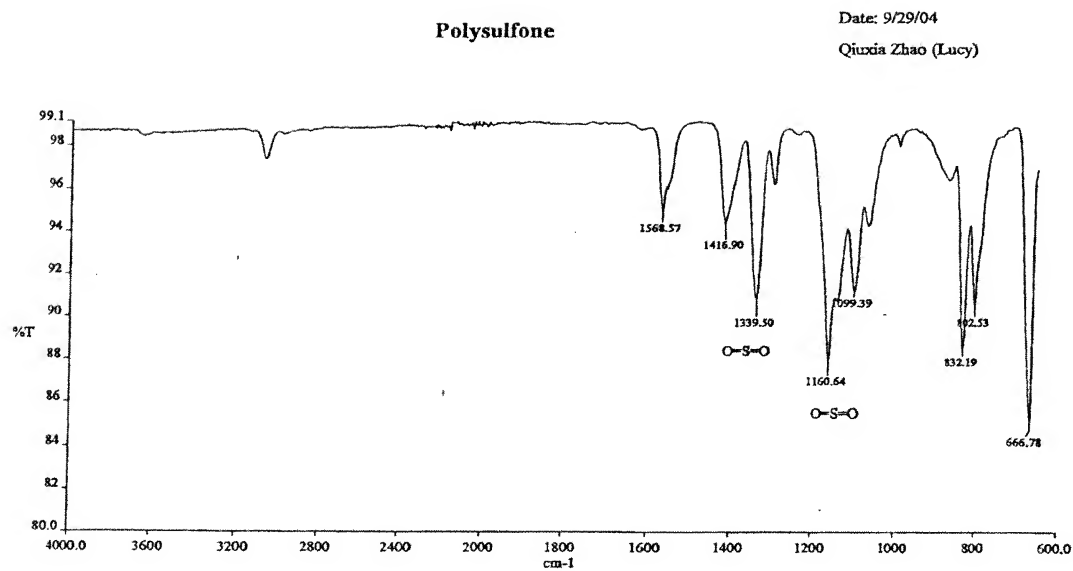


Figure 6. IR spectrum of hyperbranched poly(phenylene sulfone).

Sample: polysulfone annealing
Size: 2.2890 mg
Method: sulfide annealing
Comment: polysulfone

DSC

File: C:\DSC\lucy\polysulfone annealing.001
Operator: Lucy Zhao
Run Date: 16-Jun-04 11:01

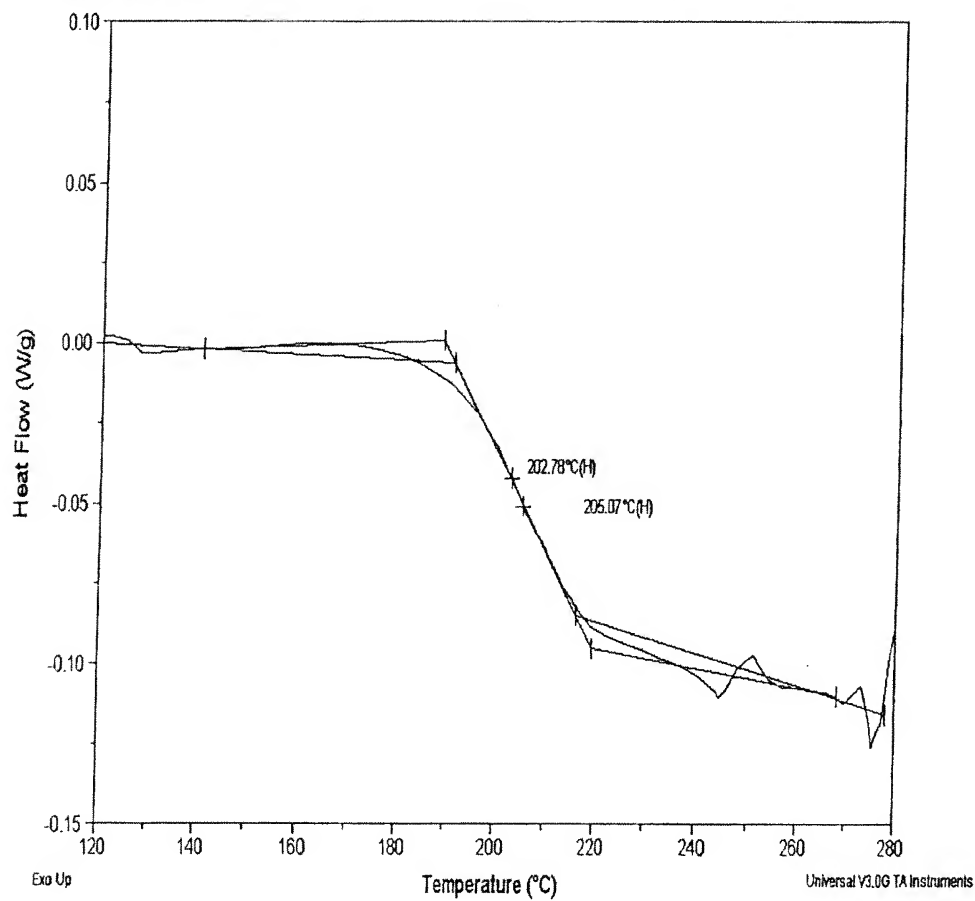


Figure 7. DSC of hyperbranched poly(phenylene sulfone).

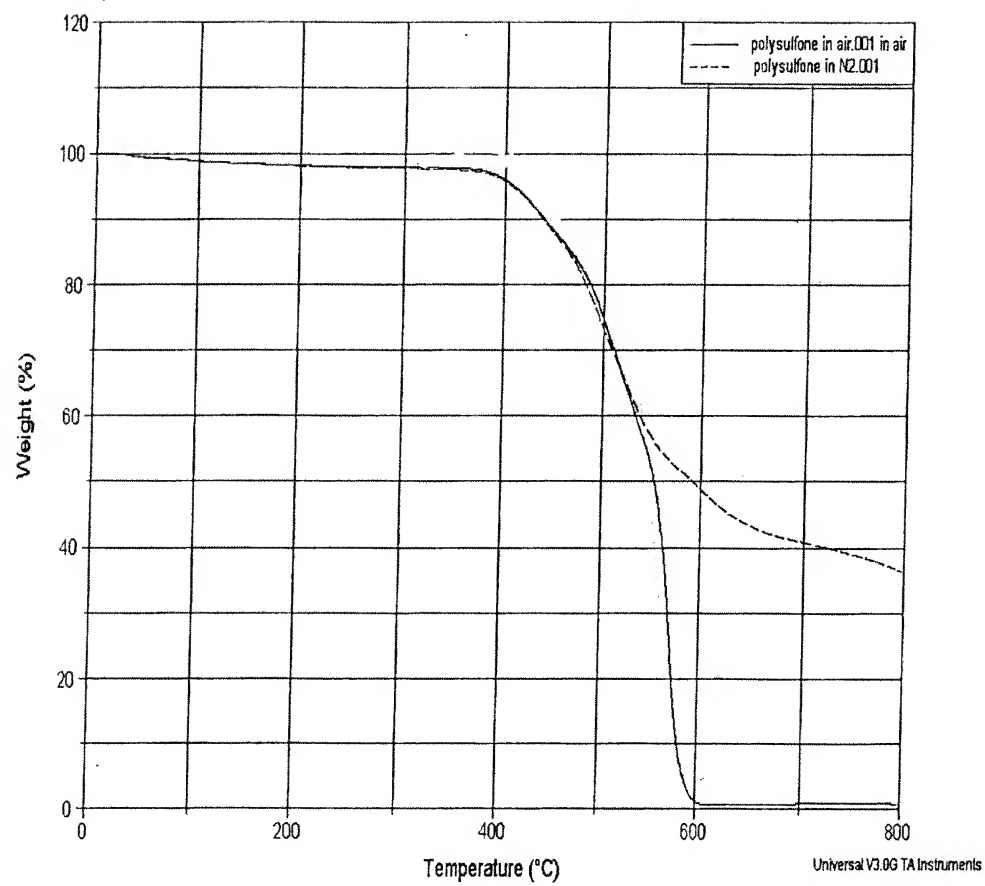


Figure 8. TGA of hyperbranched poly(phenylene sulfone) under N₂ and air atmosphere.

Sample: polysulfide with 50-1
Size: 2.6930 mg
Method: sulfide annealing
Comment: polysulfide with 50-1 core

DSC

File: C:\...DSC\lucypolysulfide with 50-1.001
Operator: Lucy Zhao
Run Date: 5-Jul-04 12:35

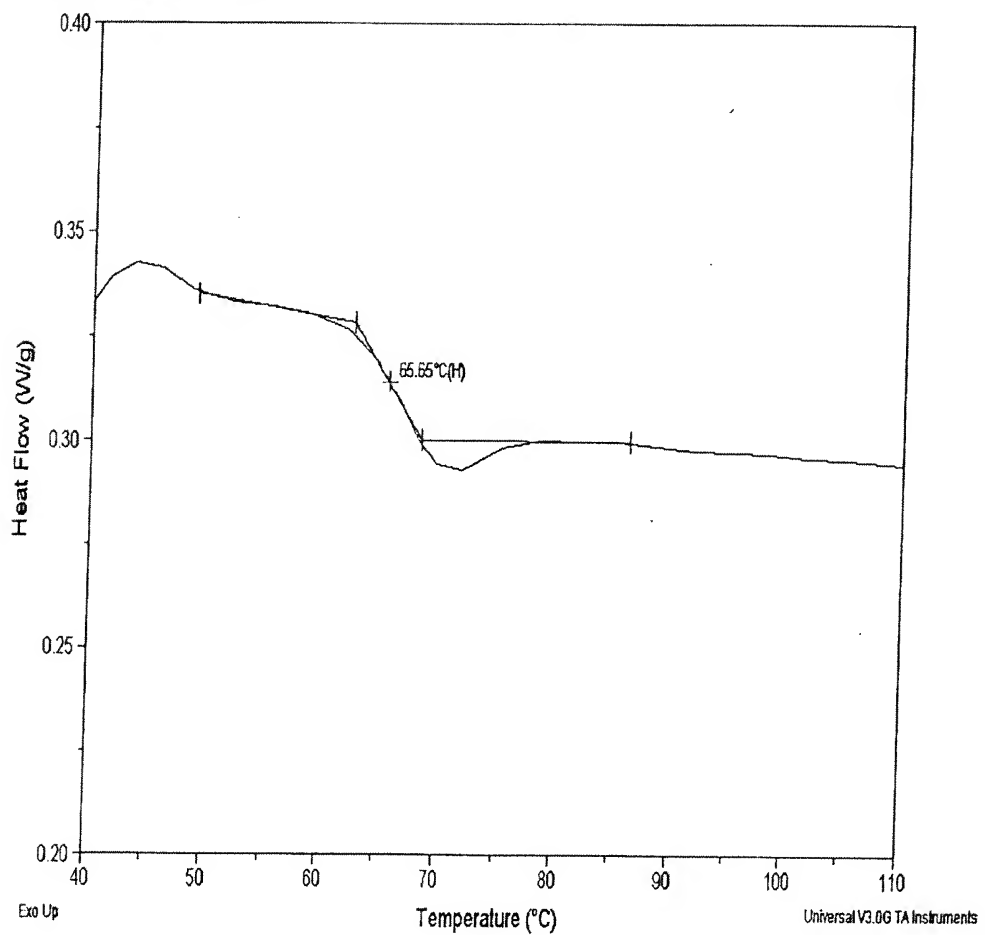


Figure 9. DSC of hyperbranched poly(phenylene sulfide) with core.

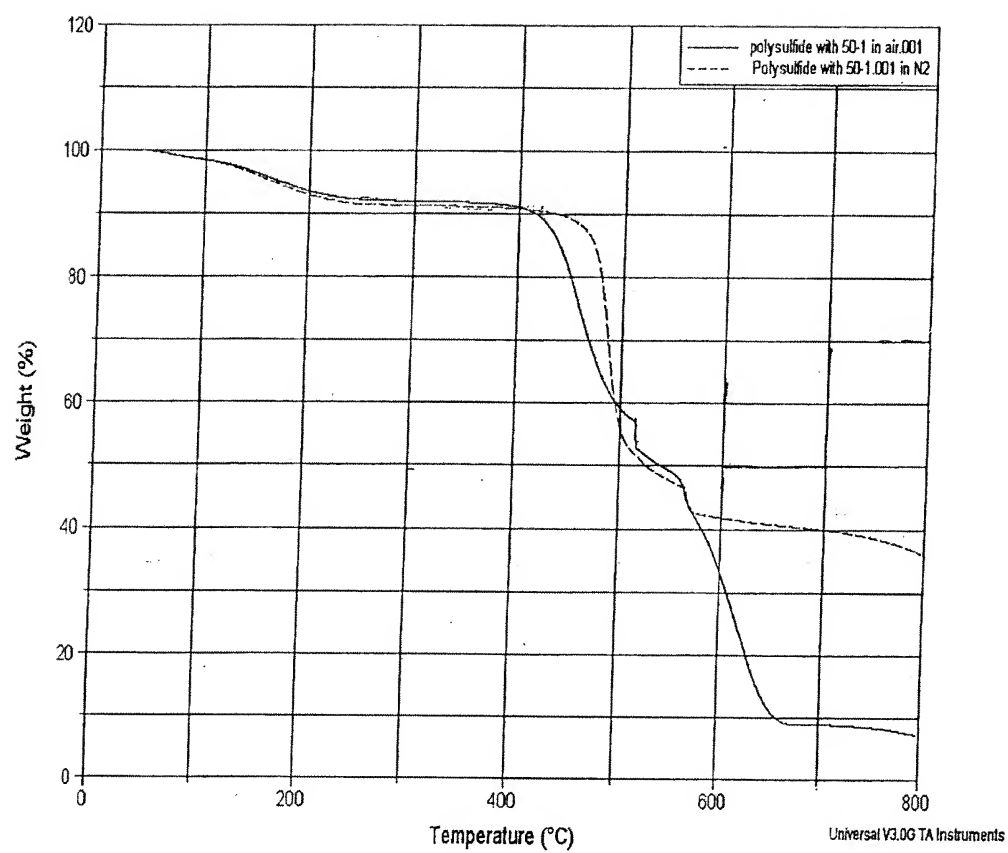


Figure 10. TGA of hyperbranched poly(phenylene sulfide) with core under N₂ and air atmosphere.

Sample: Hyperbranched PPS with End-caps
 Solvent: Acetonitrile
 Background: Acetonitrile

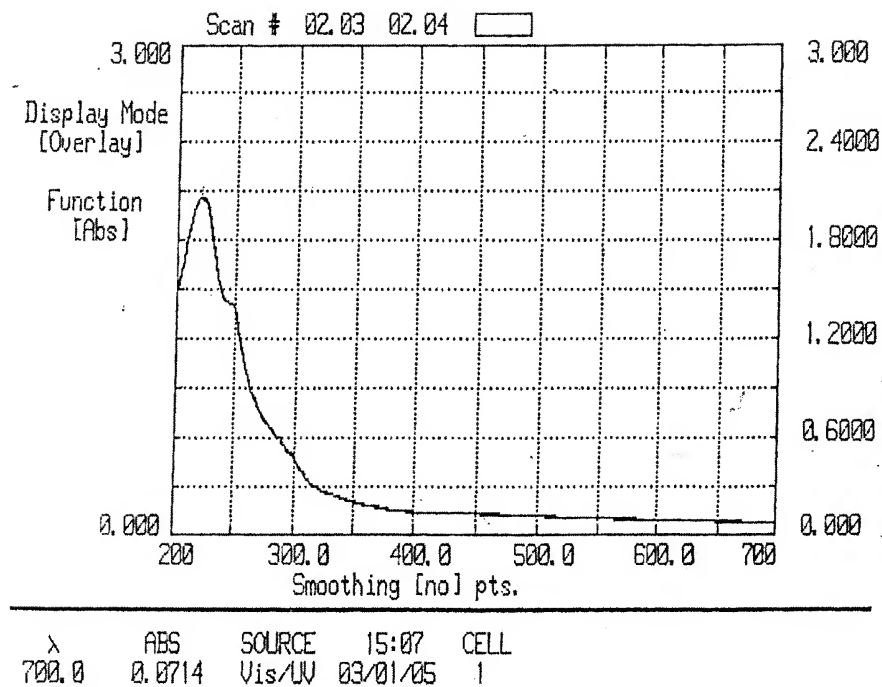


Figure 11. UV spectrum of hyperbranched poly(phenylene sulfide) with end-caps.

Sample: Hyperbranched PPS
Solvent: Acetonitrile
Background: Acetonitrile

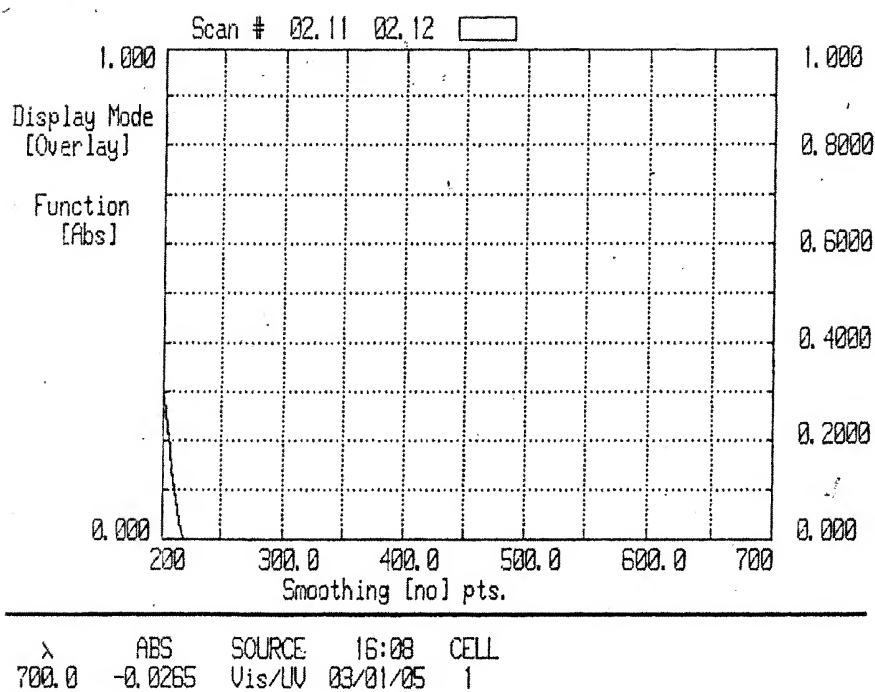


Figure 12. UV spectrum of hyperbranched poly(phenylene sulfide).

Sample: polysulfide with cap 1-1
Size: 2.0540 mg
Method: sulfide annealing
Comment: hermetic crimps

DSC

File: polysulfide with cap 1-1annealing.001
Operator: lucy
Run Date: 20-Feb-05 11:29

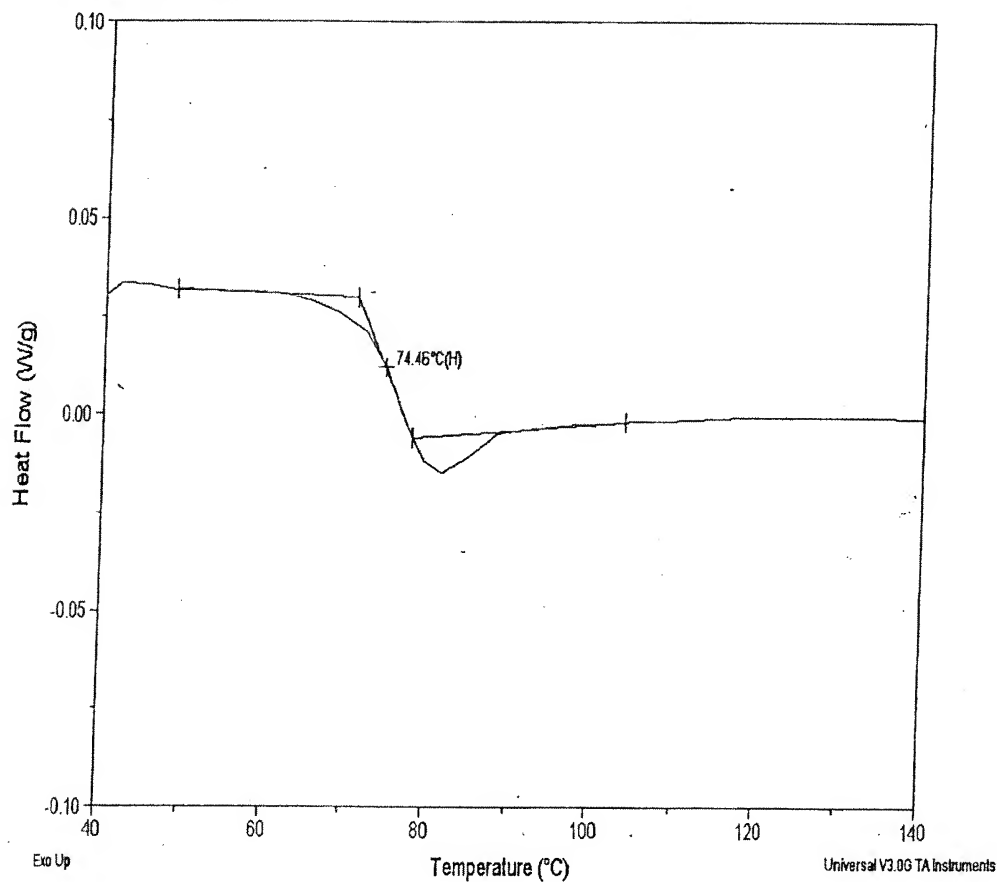


Figure 13. DSC of hyperbranched poly(phenylene sulfide) with end-caps.

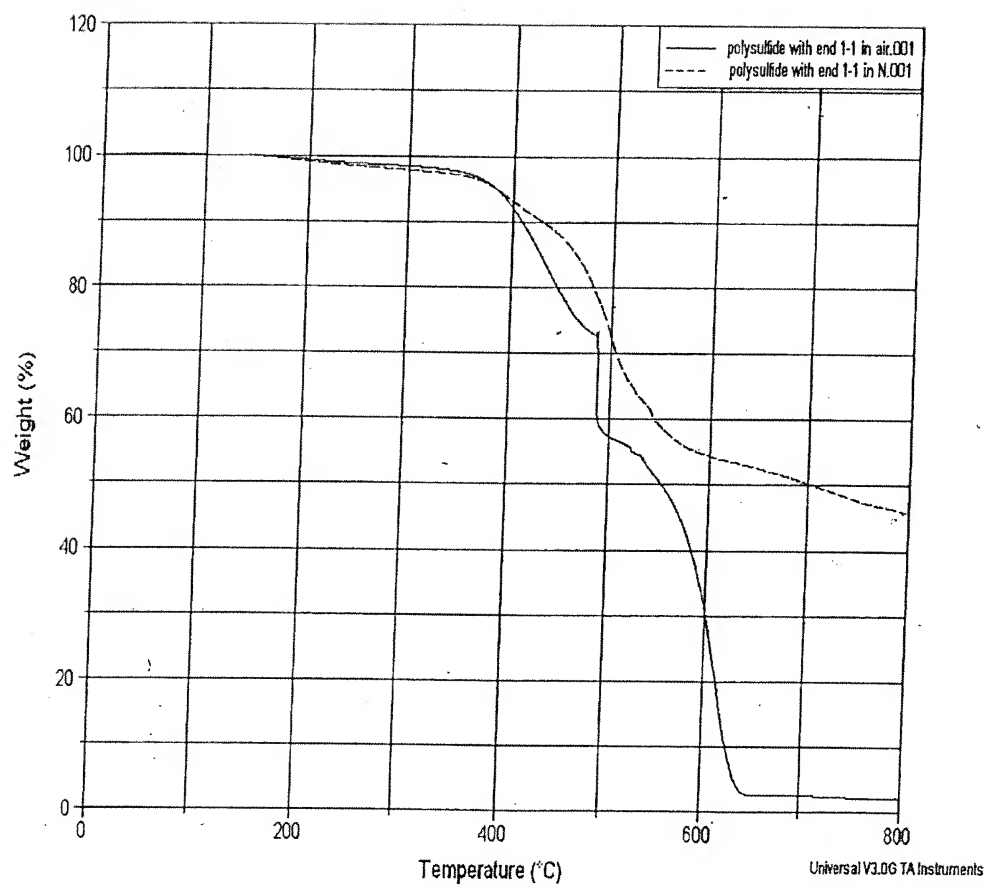


Figure 14. TGA of hyperbranched poly(phenylene sulfide) with end-caps under N₂ and air atmosphere.

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